IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of:
Michael Ludensky et al.

Application No.: 10/540,293	Confirmation No.: 8281
Filed: July 20, 2005	Art Unit: 1724
For: METHOD FOR REMOVAL OF BIOFILM	Examiner: P. A. Hruskoci

DECLARATION OF PHILIP G. SWEENY, PH.D.
UNDER 37 C.F.R. § 1.132

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

I, Philip G. Sweeny, hereby declare and state as follows:

1. I am a citizen of the United States and over the age of 21.

2. I received a B.A. in Chemistry from St. Olaf College in Northfield, MN in 1981 and a Ph.D. in Organic Chemistry from the University of North Dakota in Grand Forks, ND in 1985.

3. For over 15 years as a scientist at Lonza Inc. in Fairlawn, NJ, I have researched problems, developed products, and managed projects related to water treatment and antimicrobial applications, such as efficacious dosages, treatment modes, and mechanisms of action. During this time, my efforts have resulted in two patented and commercially successful products for use during water treatment. My curriculum vitae is attached as Exhibit A to my Declaration.

4. I am a named inventor on the above-identified application and have assigned the invention of the above-captioned application to Lonza Inc., my employer.

5. I have read and am familiar with the above-captioned application and its pending claims, as amended in the Amendment submitted herewith. The pending claims recite a method for disintegrating biofilm by adding to or forming in a medium a monochlorodialkylhydantoin, dichlorodialkylhydantoin or a mixture thereof, wherein the chlorinated hydantoin can disintegrate biofouling at a concentration in which BCDMH is unable to disintegrate the biofilm.

6. I understand that the above-captioned application is a national stage application of International Application No. PCT/US2003/017882 filed June 6, 2003. I also understand that the relevant date for evaluating obviousness of the application's pending claims is, at the very latest, this filing date.

7. In my opinion, one of ordinary skill in the art as of that date would not have expected that a monochlorodialkylhydantoin, dichlorodialkylhydantoin or a mixture thereof can disintegrate biofouling at concentrations in which BCDMH is unable to do the same as set forth in the pending claims. Until our surprising discovery that chlorinated hydantoins such as 1-chloro-5,5-dimethyl hydantoin (MCDMH) and 1,3-dichloro-5,5-dimethyl hydantoin (DCDMH) could outperform brominated hydantoins such as 1-bromo-3-chloro-5,5-dimethyl hydantoin (BCDMH), one of ordinary skill in the art would have expected that the performance of bromine containing products would outperform analogous chlorinated products during biodisintegration.

8. As a result of this generalized understanding, numerous publications and patents have issued promoting the enhanced efficacy of bromine releasing oxidants over chlorine releasing oxidants. For example,

- Macchiarolo (U.S. Patent No. 4,297,224) patented the use of BCDMH in cooling applications on the basis of surprisingly enhanced performance compared to chlorine gas (see Examples 1 and 2).

- Hight (U.S. Patent No. 5,662,940) patented an "[i]mproved biocidal composition and method for controlling biofouling...The composition comprises a hypochlorite donor and a bromide ion donor..." *See* the Abstract. The improved product was based on an observation of enhanced biocidal activity of bromine containing systems compared to

pure chlorine products. The described improvement resulted in the commercialization of a new product, Towerbrom®, consisting of a mixture of chlorinated isocyanurates and bromide ion (see Kuechler, T.C. et. Al. AWT, 1991, Exhibit B) as compared to the already well known chlorinated cyanurates.

- Sanders et al. described the addition of bromide ion to chlorine compositions to enhance performance (see U.S. Patent No. 6,303,038, Exhibit C).

- Howarth, et al. demonstrated the advantages of 1,3-dibromo-5,5-dilkylhydantoin (DBDMH) over BCDMH emphasizing the belief that bromine exceeds chlorine efficacy in aqueous systems (see U.S. Patent No. 6,641,828, Exhibit D).

9. The expectations of those of ordinary skill in the art prior to our invention were based on the knowledge that the biocidal efficacies of the protonated forms of hypohalous acids were greater than their conjugate bases and that the pKa of hypobromous acid, 8.5, was greater than that of hypochlorous acid, 7.5 (see Jolles, Z.E. Ed. "Bromine and its Compounds" Academic Press, New York, 1966, p. 706-708, Exhibit E). As a result, it was commonly believed that hypobromous acid generating products (e.g., BCDMH) would be more efficacious than hypochlorous acid generating products (e.g., MCDMH) especially at the higher pHs of 8-10 encountered in cooling systems.

10. However, in light of our unexpected discovery, it is postulated that the greater biofilm removal capacity of chlorinated hydantoins compared to their brominated analogs is a result of the greater stability of chlorinated hydantoins and, thus, biofilm penetrating potential compared to the more reactive bromine species. In other words even though BCDMH is expected to be more biocidally active, the chlorinated hydantoins provide a better balance of stability and biocidal efficacy than BCDMH with respect to biofilm removal. Furthermore, the use of chlorinated hydantoins compared BCDMH is preferred because, for example, chlorinated hydantoins are less expensive to manufacture.
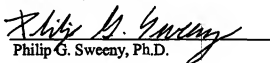
11. In summary, the state of knowledge and expectations prior to our surprising discovery was that bromine releasing oxidants would provide better microbiocidal efficacy than analogous pure chlorine systems and thus function more effectively as water treatment biocides for the

removal of biofilms. In contrast to the expectations of one of ordinary skill in the art on the effective filing date, we surprisingly discovered that pure chlorine hydantoins provide greater biofilm removal capacity than their bromine containing analogs.

       12.   I further declare that all statements made herein of my own knowledge are true, and that all statements made on information and belief are believed to be true; and further that these statements are made with knowledge that willful false statements and the like so made are punishable by fine or imprisonment or both, under §1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the instant application or any patent issued thereupon.

Respectfully submitted,

Dated: 10/1/07

Philip G. Sweeny, Ph.D.

Exhibits:

A. Curriculum Vitae of Dr. Philip G. Sweeny

B. Kuechler, T.C. et. Al. AWT, 1991.

C. Sanders Et al. "Solid Mixtures of Dialkylhydantoins and Bromide Ion Sources for Water Sanitation" US patent 6,303,038.

D. Howarth, J.N. et al. "Microbiological control in Aqueous systems" US patent 6,641,828, Nov.4, 2003).

E. Jolles, Z.E. Ed. "Bromine and its Compounds" Academic Press, New York, 1966, p. 706-708.

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Exhibit A

Philip G. Sweeny

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32 Hillside Road
Hackettstown, NJ 07840

Education:

University of North Dakota (UND) Grand Forks, ND	Ph. D. Organic Chemistry, 1985	GPA: 3.85
St. Olaf College Northfield, MN	B. A. (ACS certified) Chemistry, 1981	GPA: 3.13

Employment History:

- 1989 to date — Lonza Inc.

  Fairlawn, NJ

  2005 – 2006 Technical Specialist
  1999 - 2004 Sr. Res. Associate
  1993 - Research Associate
  1990 - Sr. Research Chemist
  1989 - Research Chemist

- 1987-89 — Energy Research Center
  Grand Forks, ND — Research Associate.

- 1986-87 — UND — Post Doctoral

Professional History:

- Discovered and developed a novel method for stabilizing chlorine, dramatically decreasing halogenated waste by-products commonly associated with papermaking. This patent forms the basis of the commercially successful Equinox® product line.

- Patented and commercialized a method for inhibiting the hydrogen peroxide decomposition enzyme catalase facilitating broader use of this environmentally favorable oxidant. This technology forms the basis of the Catagard® product line.

- Managed a product development team achieving EPA and FDA approval for hydantoin based oxidants in the papermaking industry.

- Defined the ignition profiles of pulverized coal using carbon monoxide and carbon dioxide release profiles in support of a coal combustion model for power generation boilers.

- Explored the use of laser–induced fluorescence spectroscopy (LIFS) for profiling sodium vaporization during coal combustion.

Management & Technical Specialties:

Project Management & Product Development:

- Managed several integrated project teams successfully launching multiple EPA and FDA registered products.

- Coordinated overall safety program for global R&D center.

Technical Specialties:

- Versed in water treatment (papermaking, pool & spa, cooling, and oilfield), antimicrobial applications e.g.: efficacious dosages and treatment modes, mechanisms of action and hydrolysis, limits of applicability, registration requirements, product safety and stewardship practices and compatibility requirements, a total of 16 years experience.

- Organic and physical chemistry with a concentration in photolysis methods and reactions.

Technical Committees:

- TAPPI, Chairman of Microbiological and Microbial Technical Committee

Hobbies/Interests:

- Bible study
- Gardening
- Coaching soccer

Patents

1. Ney, B., Sinden, R., Sweeny, P. G., Lutz, P. J., Borokhov, O. and Finch, S. "**Aldehyde Donors for Stabilizing Peroxides**" US 6,696,093, 2/24/04.

2. Harvey, J. H. and Sweeny, P. G. "**Feeder and Method for Preparing Aqueous Solutions Containing High Concentrations of Solid Oxidizers**" US 6,660,168, 12/12/03.

3. Ney, B., Sinden, R., Sweeny, P. G., Lutz, P. J., Borokhov, O and Finch, S. "**Method of Bleaching Recycled Papers with Hydrogen Peroxide Stabilized with a Methylolhydantoin**" US 6,432,262, 8/13/02.

4. Sweeny, P. G., Lemke, D. W., and Ludensky, M. L. "**Partially Halogenated Hydantoins in Papermaking Applications**" US 6,429,181, 8/6/02.

5. Sweeny, P. G. "**Hydantoin-Enhanced Efficacy in Pulp and Paper Applications**" US 5,565,109, 10/15/96.

6. Morlino, N., Sweeny, P. G., and Curham, B. "**Polyglycerol Antifoam Agents in Paper Processing**" US 5,429,718, 7/4/95.

Pending Patent Applications

1. Ludensky, M. and Sweeny, P.G. "**Method for Biofilm Control in an Aqueous Medium**" Filed 12/20/02

Selected Publications

1. Sweeny, P., Murray, D., and Jimenez, L. "**Anionic Compatible Quat?**" Cooling Technology Institute, Annual Convention, 2007.

2. Sweeny, P., Lammering, D., and Jimenez, L. "**Bardac® LF 18 – A Novel Cooling Water Algaecide**" Association of Water Technologists, Annual Convention, 2006.

3. Himpler, F., Sweeny, P. and Ludensky, M. "**The Benefits of a Hydantoin-Based Slimicide in Papermaking Applications**" 55th APPITA Annual Conference, 2001, Paper 1B41.

4. Sweeny, P. and Ludensky, M. "**Furnish Compatibility and Efficacy of Oxidizing Slimicides**" Proceedings of the 2001 TAPPI Papermakers Conference, 2001, Paper 17-2, 47.

5. Sweeny, P., Ludensky, M. and Borokhov, O. "**Mill Performance of a Brominated Methylethylhydantoin Slimicide**" Proceedings of the 1999 TAPPI Papermakers Conference, 1999, 437.

6. Ludensky, M. L., Himpler, F. J., Sweeny, P. "**Control of Biofilms with Cooling Water Biocides**" Corrosion 98, NACE, 1998, Paper 522 and Materials Performance, October 1998, p. 50.

7. Sweeny, P. "**Hydantoin Effects on Hypochlorite and Hypobromite Biocidal Efficacy in Alkaline Papermaking Applications**" Proceedings of the 1996 TAPPI Papermakers Conference, 1996, 529.

8. Sweeny, P. "**The Effect of N-hydrogen Compounds on Hypochlorite Biocidal Efficacy in Papermaking Applications**" Proceedings of the 1995 TAPPI Papermakers Conference, 1995, 183.

9. Sweeny, P. and Himpler, F. "**A Novel Nonoxidizing Biocide for Cooling Water Systems**" Corrosion 94, NACE, 1994, Paper 450.

10. Sweeny, P.S., Grow, D.T. "**Ignition and Combustion Characteristics of a Lignite**" Energy and Fuels, 1989, 3(6),678.

11. Sweeny, P. G., Abrahamson, H.B., Radonovich, L. J. Ballintine, T.A. "**Determination of Atomic Sodium in Coal Combustion Using Laser Induced Fluorescence**" Am. Chem. Soc., Div. Fuel Chem. Preprint, 1987, 32(4)186.

12. Montano, P.A., Stenberg, V.I., Sweeny, P.G. "**In Situ study of the Hydrogenation of Diphenyl Ether In the Presence of Pyrrhotite and H_2S**" J. Phys. Chem., 1986, 90,156.

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Exhibit B

| P⊃ |

Your comments, please
See Fig. 6

Jack

Development of Monsanto's Towerbrom ® Microbiocide, A New Bromine Microbiocide for Recirculating Water Systems

Thomas C. Kuechler, Lawrence F. Rakestraw, David F. Graham
Monsanto Company
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St. Louis, MO 63167

and

Jack V. Matson
Department of Civil and Environmental Engineering
University of Houston
Houston, TX 77004

ABSTRACT

A new family of bromine-based microbiocides, called Towerbrom®, has been developed for use in recirculating water systems. Each Towerbrom product is a solid mixture of sodium bromide and a chlorinated isocyanurate (ACL®). The compositions have been carefully chosen to provide full bromine performance at a minimum cost. This paper reviews the technology behind Towerbrom and reports the results from several field trials, comparing Towerbrom to other solid bromine and chlorine microbiocides. These trials have shown that Towerbrom performs as a bromine microbiocide and is the most cost-effective product tested.

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I. Overview of the Chemistry of Bromine Microbiocides

Monsanto has developed a family of bromine and chlorine microbiocides for the industrial water treatment market based on its ACL chlorinated isocyanurates. This family of products offers several advantages including ease of use, versatility, and superior cost performance. This paper reviews:
1) the chemistry and microbiocidal efficacies of bromine products;
2) the advantages and disadvantages of various oxidizing microbiocides; and
3) the technology involved in Monsanto's new Towerbrom microbiocides.

All oxidizing microbiocides perform two functions: 1) killing bacteria, fungi and algae; and 2) clearing the water of contaminants which are nutrients for the microorganisms, by oxidizing debris. Oxidizing debris is a major contribution to the total oxidizer demand, especially for periodic shock treatment.

Halogen oxidizers primarily attack nitrogenous materials and the more reactive organic molecules. Their ability to preferentially attack proteins allows them to be effective at low enough concentrations to minimize interaction with other treatment chemicals such as polymers and phosphonates. Their high reactivity means that they do not persist for long periods of time after being discharged, but it also means that overdosing an oxidizer can lead to corrosion, chemical interactions, or attack on wood. The halogen oxidizers are less volatile than O_2 or ClO_2, so it is easier to maintain a free residual in the water system.

There is a large body of literature on the fundamental microbiocidal and chemical properties of bromine (1-63). A number of papers have specifically addressed the use of bromine microbiocides in cooling towers (64-85). Bromine products have been used effectively since the 1940's to disinfect pools, spas, cooling water, drinking water and waste water, and new bromine products continue to be developed (86-89). Bromine products often have significant advantages over the chlorine products and in recent years have made significant inroads into markets dominated by chlorine. This trend is due to several factors.

A. Bromine versus Chlorine Microbiocides

First of all, bromine is an excellent microbiocide for a large number of bacteria (1,3,4,8,12,16,18,22,23,31-33,37,40,45,48,52-54,71,78,90), fungi (90), algae (34-36,46,64,90), amoebic cysts (56) and viruses (3-5,14,17,46,50,58). The amoebic cysts are the most difficult microorganisms to kill, followed by viruses and then bacteria (38). Because bacteria attached to surfaces as biofilms are much harder to kill than free floating bacteria (70), dispersants are often added to enhance the performance of the microbiocides (81). It is important to continuously maintain a minimum level of microbiocide, since it is easier to prevent biofilm formation than it is to remove an established biofilm.

Secondly, free bromine has microbiocidal properties which are superior to free chlorine at pH's above 8. Both hypobromous acid and hypochlorous acid behave as weak acids, dissociating in water as shown:

$$HOBr = H^+ + OBr^- \qquad\qquad pK_a \ (25°C) = 8.7 \qquad\qquad (1)$$

$$HOCl = H^+ + OCl^- \qquad\qquad pK_a \ (25°C) = 7.5 \qquad\qquad (2)$$

The microbiocidal effectiveness of each acid is very dependent on pH, decreasing at higher pH's. This indicates that the undissociated forms are the microbiocidally active species, while the hypohalite ions are much less effective. Since the pK_a for HOBr is higher, it is less dissociated at a given pH, as shown in Figure 1. Hence, bromine is more microbiocidally active, especially in the pH range of 7.5 to 9.0. This is an important range for those cooling water recirculation systems where alkaline corrosion control programs are replacing the chromate based programs which have now been banned.

Figure 1: The pH dependence for dissociation of HOCl and HOBr

Percent Un-Ionized Acid
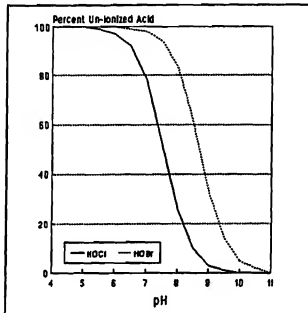
Third, hypobromous acid is more effective than hypochlorous acid in ammonia contaminated water (12,16,19,27,63,71). In the presence of ammonia, both acids form halamines such as NH_4Br or NH_4Cl. The formation of bromamines has little effect on the microbiocidal effectiveness of HOBr because the bromamines hydrolyze readily to re-release HOBr very rapidly:

$$NBr_3 + 3H_2O = 3HOBr + NH_3 \tag{3}$$

$$HNBr_2 + 2H_2O = 2HOBr + NH_3 \tag{4}$$

$$H_2NBr + H_2O = HOBr + NH_3 \tag{5}$$

In sharp contrast to the bromamines, the formation of chloramines sharply reduces the microbiocidal effectiveness of HOCl (about 0.001 times that of HOCl). This is due to the fact that the chloramines are more stable than bromamines, so that they hydrolyze very slowly to re-release HOCl. UV spectroscopy (15,21,24,26) has been used to distinguish between the various

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bromamines and chloramines and to show the rate at which equilibrium is achieved. For both bromine and chlorine, the dominant halamine species are determined by the ammonia/halogen ratio and the pH (55).

Table 1 illustrates the relative microbiocidal effectiveness of the various halogen species at different pH's. The efficacies are compared on the basis of the CT value, the product of the microbiocide concentration and the time required for 99.0% killing efficiency. Lower values for CT indicate better efficacy. Both high pH and the presence of ammonia adversely affect the killing efficiency of chlorine, while bromide addition substantially eliminates both of these negative effects.

Table 1: Summary of lab quick kill results using E. coli.

pH	Microbiocide	Concentration (mg/L, as Cl_2)	Time for 99.0% Kill (min)	CT
7.0	Free chlorine	0.1	< 1	< 0.1
7.0	Combined chlorine	1.0	9	9.0
7.0	Combined bromine	0.3	< 1	0.3
7.0	Free bromine	0.1	< 1	< 0.1
8.0	Free chlorine	0.3	1.5	0.45
8.0	Combined chlorine	2.0	8	16.0
8.0	Combined bromine	0.3	2.5	0.75
8.0	Free bromine	0.1	< 1	< 0.1
8.5	Free chlorine	0.5	2	1.0
8.5	Combined chlorine	2.0	9	18.0
8.5	Combined bromine	0.5	1.5	0.75
8.5	Free bromine	0.2	< 1	< 0.2

The difference in efficacy of the halamines is an important factor because most cooling systems are operated so that they walk a thin line between having enough free halogen in the water to prevent biofouling but not enough to cause corrosion of the costly metal components. Breakpoint halogenation, the complete elimination of all ammonia contaminants, is never obtained under these conditions. As a result, the free halogen residual is very low (0.1-0.4 mg/L) and the halamine concentration is very high (0.5-2 mg/L). Thus, bromine is preferred in cooling water because the combined halogen is also microbiocidally active. The greater effectiveness of bromine versus chlorine means that lower usage rates are needed to achieve equivalent bacteria control. The lower usage rates can more than compensate for the higher unit cost of the bromine product.

There are some cases, however, where chlorine may still be the preferred chemical. Chlorine is certainly a very effective microbiocide when the pH is controlled at a low pH, below 7.5. Chlorine may be preferred in systems exposed to strong sunlight, such as cooling ponds or fountains, since HOCl can be

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stabilized against decomposition by UV but HOBr cannot. In other cases, bromine may be preferable, but the system may lack sufficient control to realize its true cost advantages. In these cases, chlorine's inherently lower cost will be very attractive. In addition, the physical or solubility characteristics of some forms of chlorine may be preferable to the current bromine products.

When using an oxidizer as a shock treatment, most of the added halogen is used to burn out debris. Only after this demand has been met can a substantial free halogen concentration be established. Chlorine is a stronger oxidizer than bromine and the oxidizing properties of chlorine are not dramatically affected by pH. Therefore, chlorine is really preferred for the oxidizing part of the shock. Only after the demand has been met and the primary goal is killing microorganisms is bromine the desired agent.
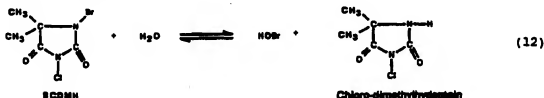
B. Methods of Generating Hypobromous Acid

There are basically two approaches to generating hypobromous acid in water. The first approach is achieved by dissolution/hydrolysis of materials containing available bromine. These materials include: 1) elemental bromine as a gas, liquid or aqueous solution (16,28,29,54,56,64,73); 2) bromine chloride (17,31,40,43,46,61); 3) perhalide salts, RX_2, where X = Br and/or Cl (48); and 4) N-bromo-imide compounds, e.g., 1-bromo-3-chloro-5,5-dimethyl-hydantoin (BCDMH) or N-bromosuccimide, according to the following reactions:

$$Br_2 + H_2O \longrightarrow HOBr + H^+ + Br^- \tag{6}$$

$$BrCl + H_2O \longrightarrow HOBr + H^+ + Cl^- \tag{7}$$

$$RBr_2 + H_2O \longrightarrow R^+ + HOBr + H^+ + 2Br^- \tag{8}$$

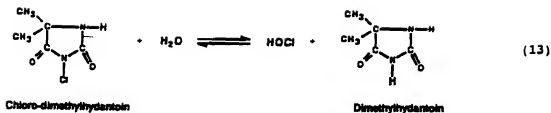$$R_2N-Br + H_2O \rightleftharpoons HOBr + R_2N-H \tag{9}$$

In the second approach, free bromine is generated by mixing appropriate amounts of bromide ion and an oxidizer capable of oxidizing the bromide to HOBr. This reaction predominates in the chlorination of seawater, which contains about 65 mg/L of bromide. Chlorine oxidizers are most commonly used (5,7,8,13,47,60), although other strong oxidizers could also be used:

$$Br^- + HOCl \longrightarrow HOBr + Cl^- \tag{10}$$

$$Br^- + H^+ + O_3 \longrightarrow HOBr + O_2 \tag{11}$$

In the case of BCDMH, hypobromous acid is generated by a combination of these two approaches. When dissolved in water BCDMH hydrolyzes to give both HOBr and HOCl (3,4,5,7,47):

$$\tag{12}$$

BCDMH   Chloro-dimethylhydantoin

$$\text{Chloro-dimethylhydantoin} \quad + \quad H_2O \quad \rightleftharpoons \quad HOCl \quad + \quad \text{Dimethylhydantoin} \tag{13}$$

The second hydrolysis step to produce HOCl (equation 13) is considerably slower than the first hydrolysis step (equation 12). During disinfection or oxidation of debris, HOBr will be consumed and bromide ions will be produced:

$$HOBr \ + \ \text{debris} \ ---> \ H^+ \ + \ Br^- \ + \ \text{waste products} \tag{14}$$

The bromide ion will then be reoxidized by HOCl to regenerate HOBr according to equation 10. The hypobromous acid is then used one more time and bromide ion is again produced (equation 14). However, at this point, the bromide is discarded since the next molecule of BCDMH already contains available bromine. Dantobrom™ contains a mixture of BCDMH and chlorinated hydantoins, so the bromine atom is used an average of 3.3 times before being discarded.

C. Pros and Cons of the Current Bromine Products

Despite the advantages of bromine over chlorine, a number of factors have slowed the transition from chlorine to bromine. In some cases, the bromine products in the marketplace did not provide the combination of convenience, cost, and safety desired.

Some of the current bromine products are inconvenient or dangerous to handle. Br$_2$ and BrCl are hazardous materials since they are both toxic, liquified gases and require careful handling to avoid leaks. Thus, they closely resemble chlorine gas and its potential problems. NaBr is often added separately to water being treated with chlorine microbiocides. This is a cost effective way to produce bromine, but is inconvenient since two chemical feeds, and thus separate feed systems, are required. Often, the NaBr is added at a stoichiometric ratio to the chlorine. This is unnecessary and increases the treatment cost. Because BCDMH is a solid, it is considerably safer to store and handle than gaseous or liquid oxidizers. However, it is only slightly soluble requiring large feeders and high water flow rates to get enough of the BCDMH dissolved. In addition, it tablets rather poorly, requiring the addition of several percent of an inert to obtain acceptable tablets. Dantobrom has a somewhat faster dissolution rate than BCDMH.

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Another disadvantage of the hydantoins is the possible effect of the 5,5-dimethylhydantoin (DMH) left over once the available halogen has been used. Zhang and Matson (85) have shown that high concentrations of DMH can degrade BCDMH's microbiocidal efficacy by combining with the HOBr and thus removing free bromine from the water. DMH/HOBr ratios over 10 should be avoided, so the DMH concentration should not exceed about 5 mg/L. DMH would be expected to greatly exceed this limit when using BCDMH, if the DMH is only removed from the water by blowdown. However, our field trial data indicates that DMH is being removed from the water in some way, since very little DMH was ever detected in the cooling water. DMH reacts with free chlorine, either chlorine or bromine, in a breakpoint-type reaction (91). Since this reaction creates a halogen demand some fraction of the available halogen in BCDMH is used to destroy the ring. This leads to higher usage rates and higher costs. This reaction occurs to a significant extent before the dissolved microbiocide even leaves the feeder, because the reaction is fastest at the high concentrations found in the feeder. This is particularly important in shock feeding practices where the feeder is shut off and the tablets sit in water for long periods of time.

Since many bromine products contain large amounts of bromine, they are more expensive and have relatively low available halogen contents, as shown in Table 2. Thus, Br_2, BrCl, and BCDMH contain 2, 1 and 0.5 equivalents of bromine per mole of available halogen. A product would be more efficient if it contained a smaller percentage of bromine but still functioned as a bromine microbiocide. This can be done by recycling the bromine, with most of the available halogen being provided by a cheaper source, such as chlorine. This is the basis for Monsanto's Towerbrom microbiocide. Table 2 also shows the percent available halogen for the Towerbrom products and some chlorine microbiocides. Towerbrom 60M has an available halogen content similar to the hydantoin materials (BCDMH and Dantobrom) while Towerbrom 90M has the highest available halogen content of any bromine product.

Table 2: Available Halogen Contents of Various Microbiocides.

Microbiocide	% Available Halogen (as Cl_2)
Br_2	44.4
BCDMH (commercial)	55
Towerbrom 60M	57
BrCl	61.5
Dantobrom *	62
Towerbrom 90M	84
Towerchlor 56	56
Calcium hypochlorite	65
DCDMH *	72
Towerchlor 90	90
Cl_2	100

* Dantobrom is a mixture of 60% BCDMH, 27% 1,3-dichloro-5,5-dimethyl-hydantoin (DCDMH), and 11% 1,3-dichloro-5-ethyl-5-methylhydantoin (DCEMH).

II. Monsanto's Towerbrom Technology

A. Product Description - Basic Chemistry and Properties

Monsanto is the world's largest manufacturer of chlorinated isocyanurates (ACL) and has extensive experience in their use in disinfection of swimming pools and spas and in cleaning, bleaching and hard surface sanitizer applications. The chlorinated isocyanurates have also been used to treat cooling water systems, where they provide chlorine performance. In the last few years, we have developed a modification which enables the chlorinated isocyanurates to perform as bromine microbiocides for use in recirculating cooling water systems.

Monsanto is now introducing a family of four oxidizing microbiocides:
 • Towerbrom 90M - Slow dissolve 3" tablets which deliver bromine performance.
 • Towerbrom 60M - Fast dissolve granules which deliver bromine performance.
 • Towerchlor 90 - Slow dissolve 3" tablets which deliver chlorine performance.
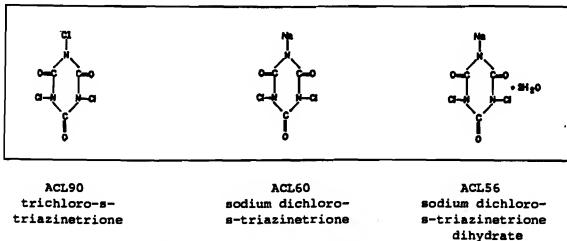 • Towerchlor 56 - Fast dissolve granules which deliver chlorine performance.
The properties of these four products are summarized in Table 3. Figure 2 shows the structures of the ACL materials on which these products are based.

The three inch Towerbrom and Towerchlor tablets work best in continuous feed systems. They can be used readily in most commercially available feeders or in most non-feeder applications (the bucket or bag approach). We can recommend several inexpensive feeders. Since the tablets contain the highest levels of available halogen of any solid oxidizing microbiocide, lower usage rates are

Table 3: Properties of the Towerbrom and Towerchlor Products

Properties	Towerbrom 90M	Towerbrom 60M	Towerchlor 90	Towerchlor 56
Composition	93% ACL90 7% NaBr	93% ACL60 7% NaBr	100% ACL90	100% ACL56
Product Form	3" Tabs	Granular	3" Tabs	Granular
Avail. Halogen (as Cl,)	84%	58%	90%	56%
Halogen Release	Fast	Fast	Fast	Fast
Solubility in 100 g H,O at 25°C	1.2 g	26 g	1.2 g	25 g
Dissolution Rate	Slow	Fast	Slow	Fast
pH, 1% Solution	3	6	3	6
NFPA Oxidizer Class	2	3	2	1

Figure 2: Structures of the ACL Components of Towerbrom and Towerchlor.

ACL90	ACL60	ACL56
trichloro-s-	sodium dichloro-	sodium dichloro-
triazinetrione	s-triazinetrione	s-triazinetrione
		dihydrate

required to provide the same level of biofouling control. A lower usage rate
means that feeders must be refilled less often, and reduces service time and
shipping costs. Although the 3" tablets are "slow dissolving", their
dissolution rate is twice that of 1" BCDMH tablets and very similar to Dantobrom
briquettes, despite the larger tablet size. Due to their non-spherical shape,
the dissolution rate is more uniform over time than that of 1" tablets. The
tablets are also quite hard, and therefore resistant to damage during shipping.

The granular products, Towerbrom 60M and Towerchlor 56, are ideally suited for
intermittent or shock dosing. They are easily fed by hand and dissolve in
minutes. They have the added benefit of a neutral pH to minimize corrosion and
they do not contain any hardness ions. Towerchlor 56 microbiocide is a Class 1
oxidizer and therefore does not require a DOT oxidizer label.

Field trials have shown that Towerbrom is an effective, low cost way to obtain
bromine disinfection performance when used in either a low level, continuous
feed practice or a shock dosing practice. Towerbrom can do this with only small
amounts of bromide because it is capable of simultaneously supplying free
chlorine and bromide to the water at rates so that the stoichiometries of the
following reactions are satisfied under most application conditions:

$$HOCl + Br^- = HOBr + Cl^- \qquad \Delta F_{rn} = -7,566 \text{ cal} \qquad (15a)$$
$$K_{eq} = 9.55 \times 10^5$$

$$OCl^- + Br^- = OBr^- + Cl^- \qquad \Delta F_{rn} = -5,826 \text{ cal} \qquad (15b)$$
$$K_{eq} = 1.96 \times 10^4$$

The high negative free energies and equilibrium constants for these reactions
indicate that they occur readily and that the bromine forms are heavily favored.

To operate as completely bromine microbiocides, the Towerbrom products must be
able to maintain at least one mole of bromide in the water for each mole of free
chlorine. To do this, the mole ratio of the sum of all bromine-containing
species (HOBr, OBr⁻, Br⁻) to the sum of all free halogen species (HOBr, OBr⁻,

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HOCl, OCl⁻) present in the water must be higher than one. This ratio is a convenient way to express the extent of conversion of free chlorine to free bromine (92). It is also a convenient way to establish if a composition is performing as a bromine microbiocide. The type of performance obtained depends on the mole ratio maintained in the water, rather than on the ratio in the microbiocide before it is added to the water. A mole ratio of 1.0 corresponds to a Br⁻/Cl, weight ratio of 1.127, so the ratio of the bromide concentration (in mg/L) to free halogen concentration (in mg/L as Cl₂) should be at least 1.127.

The literature (13) and our experience indicate the reactions in equation 15 occur quickly, despite the low concentration of the two reactants. For typical cooling tower applications, where the free halogen concentration is 0.1-0.5 mg/L and the bromide concentration is about 1-5 mg/L, the reaction half life is 1-10 minutes. The reactions continue to proceed to completion as long as some bromide ion is present. The reaction half life is generally shorter than the mixing time of most cooling systems, and is much smaller than the lifetime of the microbiocide in the water. Thus, as long as the Towerbrom products provide enough bromide to the water, the free chlorine will be converted to free bromine and the products will perform as bromine microbiocides.

B. Bromide Buildup and Recycle

The patent and technical literature allude to methods (8,9,52,64-69,71-84) and compositions that supply the bromide and free chlorine in stoichiometric ratios. These approaches are not the most efficient since they result in excessive use of bromide. Towerbrom microbicide works because the bromide builds up in the water so that it can be used over and over, as diagrammed in Figure 3. Because bromide is continuously recycled around the loop, the amount of bromide added must only make up for the amount lost. Thus, the amount of bromide donor required to make a Towerbrom composition perform as a bromine microbiocide is only 4-7 wt% of the composition, a quantity significantly less than the stoichiometric ratios espoused by other investigators. The following example and Figure 4 illustrate how the Towerbrom microbiocides work.

Example: Towerbrom 90M (93 wt% ACL90 and 7 wt% NaBr) is continuously fed to a cooling tower which contains no bromide initially. The ACL90 generates HOCl and the NaBr releases bromide ions, which are quickly oxidized to HOBr and OBr⁻. Since only 0.083 mg/L of bromide is added per mg/L of free chlorine, the bromide concentration is initially very low, and the composition behaves as a chlorine microbiocide. As free halogen is consumed by demand, more microbiocide must be added. Initially, the bromide concentration increases rapidly with each addition since the bromide addition rate is significantly larger than the bromide loss rate, even though a fraction of the bromide will be lost from the system by blowdown and other losses. As the bromide concentration builds up, the fraction of free halogen which exists as free bromine grows larger and the bromide loss rate increases. The bromide concentration will increase as long as the Towerbrom composition supplies bromide at a rate exceeding the bromide loss rate. Eventually, the bromide loss rate increases until it equals the bromide addition rate. At this point, a steady state condition is established and the bromide concentration remains constant. If the Towerbrom composition is capable of building the bromide concentration to a high enough level, where the Br⁻/Cl, mole ratio exceeds 1.0, the composition will perform as a bromine microbiocide.

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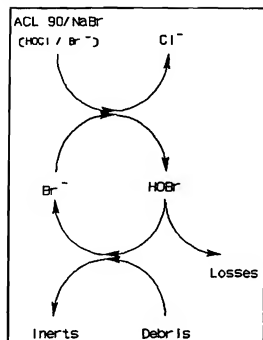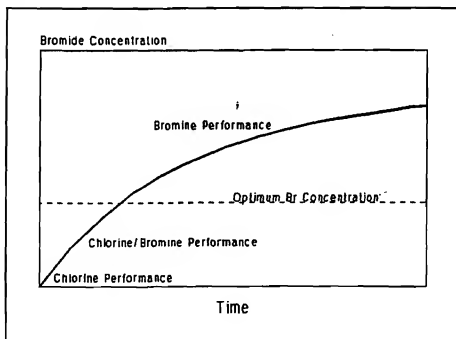**Figure 3: Schematic of Bromide Recycle Loop**

Figure 4: Schematic of the buildup of bromide ion as described above.

Initially, it was believed that blowdown would be the only significant bromide loss. However, initial field trials revealed additional pathways for bromide loss. Further investigation demonstrated that it is necessary to compensate for losses by: -1) volatilization of hypobromous acid, 2) volatilization of bromamines, and 3) formation of organobromine compounds. Work at the Univ. of Houston (93) and elsewhere (94) has focused on measuring the Henry's Law Constant for HOBr, thereby quantifying its loss by volatilization. Although measurement of the Henry's Law Constants for the bromamines is difficult (93, 94), it is clear that the bromamines are quite volatile. If formed, they survive only a few passes through the tower before being stripped into the air.

A computer program was developed to model the bromide dynamics in a recirculating water system. The model calculates the steady state bromide concentration achieved based on the bromide feed and loss rates. The model shows that the buildup of bromide is quite rapid. In contrast to the Towerbrom results, the model shows that much higher levels of bromide are built up when using BCDMH. This is not surprising since the bromide content of BCDMH is equivalent to a 60% ACL90/40% NaBr mixture. High bromide concentrations (>10 mg/L) were also observed in the BCDMH field trials, as predicted by the model.

C. Defining the Commercial Composition

The optimum composition of an ACL/NaBr blend can be found using: 1) the halogen demand of the cooling system, 2) the available chlorine content of the ACL component, and 3) the bromide loss rate. The halogen demand of a cooling tower can be determined by operating experience or can be estimated with the equation:

$$CD = 2 \text{ ppm/day} \times 8.3 \times 10^{-4} \times (SV + DM) \tag{16}$$

where: SV = volume of recirculation system, gal
       DM = daily makeup, gal
       8.3 = conversion factor, gallons to pounds

The bromide loss rate (%/day) can be determined in several ways, and this was done in the field trials. The bromide loss rate will always be at least as large as the blowdown rate (%/day). In some of the field trials the bromide loss rate was found to be considerably higher than the blowdown rate, indicating that volatilization losses can also be important, particularly at higher free halogen levels. Blowdown rates and other losses can vary over a wide range. The bromide loss rates found in the field trials ranged from 15 to 150 %/day.

The purpose of such calculations was not to find the best composition for each tower. It is impossible to market several compositions and then expect the user to buy the right one. Instead, the calculations defined the compositions needed in a variety of situations. In this way, compositions were chosen which contain sufficient bromide to provide bromine performance for most conditions, without sacrificing too much in the way of available halogen content or cost. Modeling showed that a 7% NaBr/93% ACL90 blend provides more than enough bromide for most recirculating systems. The 7% NaBr/93% ACL60 blend has an even higher bromide to available halogen ratio and covers even more cases. The result of all of the calculations and field trials was the decision to market blends of 7% NaBr with either ACL90 or ACL60 as the best compositions to meet most situations.

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III. Field Trials

A. General Description and Analytical Methods

The theory presented above is useful for a full understanding of how Towerbrom works. However, it was also important to experimentally demonstrate that the Towerbrom products behave as the theory predicts. Several field trials were conducted comparing the performance of Towerbrom and Towerchlor microbiocides with other oxidizing microbiocides. The goal of the field trials was to:
  1) demonstrate that Towerbrom and Towerchlor are effective microbiocides;
  2) demonstrate that the Towerbrom products provide enough bromide to function as bromine microbiocides;
  3) demonstrate that Towerbrom generates free bromine under typical conditions;
  4) measure the relative usage rates of the various microbiocides;
  5) demonstrate how easily Towerbrom and Towerchlor microbiocides can be used in different feed systems;

The eight cooling towers used in the field trials are described in Table 4. In Trial 1, the microbiocides were compared at the same free halogen concentration. In the remaining trials, the feed rates and target free halogen concentrations were varied in order to compare the usage rates of the microbiocides at the same level of bacteria control. Except for Trial 4, bacteria populations were monitored with agar plate count methods. The microbiocides were continuously fed at low levels to facilitate the performance and usage rate measurements.

The Br^-/Cl_2 mole ratio was determined by: 1) measuring the free halogen concentration; 2) measuring the total concentration of bromine in all of its forms; and 3) dividing the results from steps 1 and 2:

$$\text{Mole Ratio} = [Br^-]/(FAH \times 1.127) \qquad (17)$$

    where: $[Br^-]$ = total bromine concentration, as bromide, mg/L
           FAH = free halogen concentration, as chlorine, mg/L
           1.127 = ratio of mole weights, bromide to chlorine

The free halogen concentration can be measured with a variety of techniques, ranging from simple test kits to automated analyzers. These methods measure the total oxidizing equivalents dissolved in the water and do not distinguish between free bromine and free chlorine. Therefore, the free halogen concentration measured is really the sum of the free chlorine and free bromine concentrations expressed in terms of free chlorine.

The bromide concentration can also be measured by a variety of techniques including colorimetric, ion chromatographic and ion selective electrode methods. Since all species containing available bromine are reduced to bromide ion prior to the measurements, these methods determine the concentration of bromine in all its forms, which is the quantity desired in equation 17. Colorimetric methods for bromide are particularly simple, less costly and can be portable so they can be run in the field. The preferred colorimetric method is quite selective for bromide and has a detection limit of about 1.0 mg/L (95). A Monsanto-modified version has a lower detection limit of about 0.2 mg/L. Details of the colorimetric and IC methods can be obtained from the authors.

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Table 4: Brief Descriptions of the Towerbrom Field Trials.

Trial	Volume (kgal)	Tower Type	Feeder System	Microbiocides Tested	pH
1	4	Comfort	ACL and NaBr fed separately to vary ACL/NaBr ratio.	BCDMH Towerchlor 56 Towerbrom	8.5
2	25	Comfort	Erosion feeder	BCDMH Towerbrom 90M	8.4
3	25	Comfort	Basket	BCDMH Towerchlor 90 Towerbrom 90M	8.5
4	9	Industrial	Erosion feeder	Dantobrom Towerbrom 90M	7-8
5	90	Comfort	Erosion feeder	BCDMH Towerbrom 90M	8.4
6	60	Comfort	Erosion feeder	Dantobrom Towerbrom 90K*	8.7
7	240	Industrial	Erosion feeder	BCDMH Towerbrom 90M	8.0
8	350	Industrial	Erosion feeder	BCDMH Towerbrom 90M	8.0

* Towerbrom 90K was an experimental composition with 20% KBr/80% ACL90.

It was also important to demonstrate that bromide and free chlorine actually react to generate free bromine. The analytical technique for doing this, referred to here as the Palin method (96), is a simple modification of the methods for measuring free halogen. Glycine is added before the free halogen measurement to distinguish between free chlorine and free bromine. Glycine reacts rapidly with free chlorine according to the following equation:

$$NH_2-CH_2-COOH \ + \ HOCl \ ---> \ Cl-NH-CH_2-COOH \ + \ H_2O \tag{18}$$
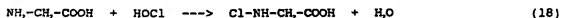
The chlorine is strongly combined and no longer responds as free halogen, while bromine is only weakly bound and still responds as free. Thus, once glycine has been added, any free halogen is recorded as free bromine. This method is applicable to the amperometric, DPD and FAS procedures for free halogen. The only drawback is that the very low levels of free halogen often used in cooling towers, say 0.1 mg/L, are close to the detection limit. Accurately dividing this small amount between free chlorine and free bromine is rather difficult.

B. **Demonstration of Bromine Chemistry**

An important objective of the field trials was to measure the concentration of bromide maintained. Table 5 summarizes the data found for the various microbiocides. No data is given for Trials 7 and 8 since the makeup water contained enough bromide to obscure the results. Towerbrom 90M provided more than enough bromide in all cases, in fact, the bromide concentration ranged from 7 to 15 times that required. The material used in Trial 6 had a higher bromide content, and this is reflected in the higher concentration found. In contrast, the hydantoin microbiocides maintained a very high bromide concentration. With Dantobrom, a bromide concentration 80X the level required was found, while BCDMH had a 60-280 fold excess of bromide.

The Palin method was used in Trials 5 and 6 to find whether Towerbrom produced free bromine. In both trials, most of the free halogen was present as free bromine, showing that free chlorine and bromide were reacting as predicted. The microbiocidal efficacy and usage rates found in the field trials, as described below, also demonstrated that Towerbrom performed as a bromine microbiocide.

Table 5: Bromide Concentration Data for the Towerbrom Field Trials

Trial	Microbiocide	Average Free Halogen (mg/L, as Cl_2)	Average Bromide (mg/L)	Br^-/Cl_2 Ratio Found
2	Towerbrom 90M	0.07	1.1	14
		0.20	1.6	7
	BCDMH	0.04	11.4	228
		0.13	12.1	81
		0.27	18.5	62
3	Towerbrom 90M	0.04	0.94	20
	BCDMH	0.10	12.5	117
		0.14	13.3	83
4	Towerbrom 90M	0.07	0.64	8
	Dantobrom	--	--	--
5	Towerbrom 90M	0.06	0.73	11
		0.13	2.3	15
	BCDMH	0.04	12.3	287
6	Towerbrom 90K	0.08	3.8	41
	Dantobrom	0.07	6.0	81

C. Efficacy Results

The killing efficiencies of bromine and chlorine were compared in two ways besides the results presented above in Table 1. The first used a dynamic laboratory apparatus called a chemistat to investigate the effect of different Br^-/Cl_2 mole ratios. The results of these experiments, Figure 5, again show that the killing efficiency of HOBr is considerably better than that of HOCl at a pH of 8.0. The killing efficiency increased linearly from a ratio of zero to a ratio of one and then leveled off. This is the result expected based on the difference in pK_a's of the two acids, assuming no enhancement of performance for a mixed microbiocide. Even though it behaves as a bromine microbiocide, BCDMH was no more effective than chlorine under these test conditions. The BCDMH results were unexpected since the free halogen concentrations were controlled at the same level, so that the killing efficiency of BCDMH should be equal to that of the high bromide Towerbrom mixture. The explanation appears to be that the presence of DMH adversely affected the microbiocidal activity (85).

The efficacies were also compared in Field Trial 1, where chlorine and bromine were compared at the same free halogen concentration. In this Trial, the free halogen concentration was controlled at 0.5 mg/L (as chlorine) using a Hach CL17 controller. The results are summarized in Figure 6. Towerbrom microbiocide achieved considerably better control than Towerchlor or BCDMH at pH 8.5, consistent with the lab results. The Field Trial results also showed that BCDMH gave even poorer control than Towerchlor, again confirming the lab results.

Figure 5: Effect of the Br^-/Cl_2 mole ratio on killing efficiency from dynamic lab experiments, using a culture of wild organisms. Conditions: 0.5 mg/L free halogen (as Cl_2), pH = 8.0.
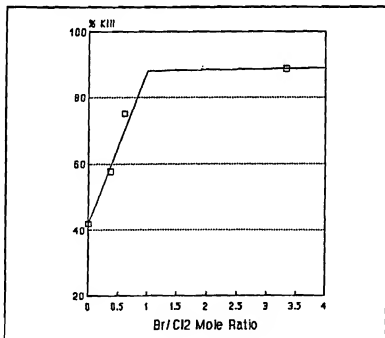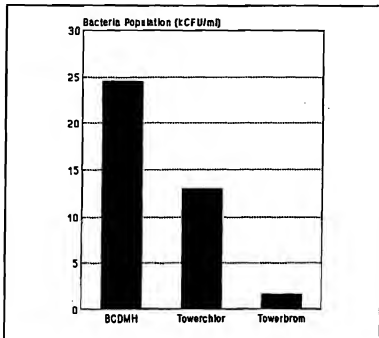
Figure 6: Summary of Killing Efficiency Results from <u>Field Trial 1</u>. All microbiocides were controlled to 0.5 mg/L free halogen (as Cl_2).

$pH = 8.5$

D. <u>Relative Usage Rates and Cost Performance</u>

Field trials 2 - 8 compared the usage rates of the various microbiocides at a given microorganism population, since the usage rate determines the cost performance. Each trial ran over a period of several weeks or months to establish accurate usage rates. Whenever possible, the usage rates were compared at similar conditions, particularly at similar heat loads, since usage rates vary widely at different loads.

Since Towerbrom 90M (84% available halogen) performs as a bromine microbiocide, it is predicted to have a lower usage rate than BCDMH (55% available halogen) or Dantobrom (62% available halogen), because of the higher available halogen content. The predicted usage rate for Towerbrom 90M is 65% (55/84) of the BCDMH usage rate or 74% (62/84) of the rate for Dantobrom. Furthermore, if the difference in killing efficiency seen in Trial 1 is important, the relative usage rate for Towerbrom 90M will be even lower. Towerbrom 90M was also expected to have a lower usage rate than Towerchlor 90, despite Towerchlor's slightly higher halogen content (90% vs 84%), since the trials were done at higher pH's.

The relative usage rate results are given in Table 6. Trials 2 and 3 are probably the most accurate field trials since they were the longest and best controlled of the trials. Trial 4 was the least well controlled and is the least accurate. A relative usage rate was not determined in Trial 5 since the BCDMH usage rate could not be established in the time allowed.

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Table 6: Usage Rate Results from the Towerbrom Field Trials

Trial	Microbiocide	Relative Usage Rate Predicted* (%)	Relative Usage Rate Found (%)
2	Towerbrom 90M vs BCDMH	65	56
3	Towerbrom 90M vs BCDMH	65	48
	Towerbrom 90M vs Towerchlor 90	111	45
4	Towerbrom 90M vs Dantobrom	74	76
5	Towerbrom 90M vs BCDMH	65	--
6	Towerbrom 90K vs Dantobrom	85	75
7	Towerbrom 90M vs BCDMH	65	45
8	Towerbrom 90M vs BCDMH	65	67

* The relative usage rate is defined as the Towerbrom usage rate divided by
the usage rate of the other microbiocide. The predicted relative usage rate
is based on the relative available halogen contents.

In Trials 4 and 8 the relative usage rate found for Towerbrom 90M was within
experimental error of that expected. In Trials 2, 3, 6 and 7 the Towerbrom
usage rates were even better than expected indicating some detrimental effects
from DMH. An accurate usage rate could not be established for BCDMH in Trial 5.
BCDMH did not control the bacteria population during a period of very hot
weather, while Towerbrom 90M rapidly brought the bacteria population under
control. This was possible because of Towerbrom's higher dissolution rate.

Trial 3 also showed that the usage rate for Towerchlor 90 was twice that of
Towerbrom 90M, demonstrating that Towerbrom 90M was behaving as a bromine
microbiocide. Towerbrom's target for free halogen concentration was lower than
the target for Towerchlor in order to achieve the lower usage rate found. Note
that the usage rates for Towerchlor 90 and BCDMH were nearly equal in Trial 3.
This indicates that the performance advantage of bromine was offset by the
higher available halogen content of Towerchlor 90. BCDMH actually required a
higher free halogen concentration than Towerchlor microbiocide to achieve the
same level of control, consistent with the results seen in Trial 1.

In several Trials, the water was analyzed for DMH. Very little DMH was found in
Trials 2 and 3 (1-7 mg/L) compared to the 24-48 mg/L which was expected based on
the bromide concentration found. In Trials 5 and 6, no DMH was detected at all
(<1 mg/L) even though 20-30 mg/L of DMH was expected. In contrast, the cyanuric
acid released from Towerbrom microbiocide was found at the expected levels
indicating no further reaction of the cyanuric acid.

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Overall, the performance observed for the Towerbrom and Towerchlor microbiocides was very much as expected. What was surprising was the performance seen for BCDMH, which was significantly lower than expected in many cases. The full effect of DMH on the BCDMH usage rate needs further study.

IV.   Summary

Both Towerbrom and Towerchlor microbiocides have been shown to be highly effective and cost efficient microbiocides for use in industrial water treatment programs. The family of four products offers versatility and ease of use.

Choosing which Towerbrom or Towerchlor product is best for a given situation depends on the feed system to be used, the pH of the water, the degree of control possible and the operating conditions of the water system. In general, Towerbrom microbiocide is preferred over Towerchlor microbiocide for systems at high pH (over 8.0) which have sufficient control to realize the cost-performance possible. When feeding the Towerbrom products on a continuous feed basis, a recirculating water system of about three cycles of concentration or more is required to achieve full bromine performance. For systems with low pH, low cycles of concentration or poor control one of the Towerchlor products may be preferable. Towerchlor microbiocide would also be preferred over Towerbrom microbiocide for cooling ponds or decorative fountains where the high exposure to strong sunlight leads to higher usage rates for the bromine product. The tabletted products, either Towerchlor or Towerbrom, are the best form for low-level, continuous feeding while the fast dissolve, granular products are best suited for shock dosing.

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For: METHOD FOR REMOVAL OF BIOFILM   Examiner: P. A. Hruskoci

DECLARATION OF PHILIP G. SWEENY, PH.D. UNDER 37 C.F.R. § 1.132

Exhibit C

(12) **United States Patent** (10) **Patent No.:** **US 6,303,038 B1**
  Sanders et al. (45) **Date of Patent:** **Oct. 16, 2001**

(54) **SOLID MIXTURES OF DIALKYLHYDANTOINS AND BROMIDE ION SOURCES FOR WATER SANITIZATION**

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(57) **ABSTRACT**

A water soluble dialkylhydantoin and a source of bromide ion are added to a body of water needing sanitization. This is followed by contacting the body of water with an oxidizing agent, which creates biocidal species in situ in the body of water.

42 Claims, No Drawings

SOLID MIXTURES OF DIALKYLHYDANTOINS AND BROMIDE ION SOURCES FOR WATER SANITIZATION

TECHNICAL FIELD

This invention relates to water sanitation methods which utilize dialkylhydantoins, bromide ions, and oxidants for bromide ions.

BACKGROUND

There is a need for disinfection and sanitization of a large number of types of bodies of water, including, for example, cooling water systems, pasteurizing systems, waste water effluents, pulp and paper mills, swimming pools, hot tubs, spas, fountains, water attractions, oil fields, air washers, fire reservoirs, and evaporative condensers. In these bodies of water, the growth of bacteria, fungi, algae, slime, and mollusks are undesirable and/or detrimental. Unfortunately, these systems often have ideal conditions for growth of these organisms. Many methods for preventing and killing such growths have been devised.

Many of these methods for sanitizing bodies of water have a drawback. For example, the use of trichloroisocyanuric acid by itself as a sanitizing chemical poses problems because trichloroisocyanuric acid reverts to chloride ion and cyanuric acid upon performing biocidal chemistry; cyanuric acid can build up to levels where the hypochlorite is rendered less effective, causing the phenomenon known as "chlorine lock." Halogenated hydantoins, which are common water-sanitizing chemicals, are notorious for their dusts, which are irritating to human mucous membranes. Hypobromous acid is a desirable biocide because it is known to be more effective than hypochlorous acid at the conditions of most bodies of water needing sanitization. Hypobromous acid is usually produced in situ due to its instability in water. Methods to produce hypobromous acid in situ have included the use of a bromide ion source and an oxidant, such as hypochlorous acid or hypochlorite ion. Further, it is known that the hypobromous acid (or whatever biocidal bromine species is formed) may be stabilized in the presence of a suitable chemical. For example, Mines de Potasse, in GB 1,358,617, use dimethylhydantoin to prolong the life of the biocidal bromine species; the biocidal bromine species only remained for several hours.

Thus, it is clear that there are several unmet needs in known water sanitization methods. A method which either prevents or circumvents chlorine lock is needed. A need exists for a method of dosing halogenated hydantoins to a body of water which minimizes the exposure of the human handler to the halogenated hydantoins. Additionally, a method for stabilizing biocidal bromine species for longer periods of time is also desirable.

SUMMARY OF THE INVENTION

This invention is deemed to satisfy all of these needs in a highly efficient and novel way. The sanitization methods described herein function in bodies of water with conditions corresponding to chlorine lock, do not expose human handlers to halogenated hydantoins, and stabilize biocidal bromine species for periods of weeks.

In one embodiment, this invention provides a method for sanitizing a body of water which comprises introducing into the body of water in the range of from about 0.15 to about 0.70 millimole per liter of a water soluble dialkylhydantoin wherein the alkyl groups are the same or different and each

alkyl group contains 1 to about 6 carbon atoms, and in the range of about 0.090 to about 0.39 millimole per liter of a water soluble source of bromide ion. An amount of an oxidizing agent capable of oxidizing the bromide ion in situ is also provided to the body of water.

Another embodiment of this invention entails a method for sanitizing a body of water. The method comprises introducing into the body of water ingredients comprising (i) a composition which comprises a solid mixture of a water soluble dialkylhydantoin wherein the alkyl groups are the same or different and each alkyl group contains 1 to about 6 carbon atoms, and a water soluble source of bromide ion, wherein the molar ratio of water soluble dialkylhydantoin to source of bromide ion in the mixture ranges from about 1.2:1 to about 7.2:1, and (ii) an oxidizing agent.

Still another embodiment of this invention provides a method for sanitizing a body of water, the method comprising introducing into the body of water (i) a composition which comprises a solid mixture of a water soluble dialkylhydantoin wherein the alkyl groups are the same or different and each alkyl group contains 1 to about 6 carbon atoms, and a source of bromide ion, wherein the molar ratio of water soluble dialkylhydantoin to source of bromide ion in the mixture ranges from about 1.2:1 to about 7.2:1, and (ii) an oxidizing agent. This method further comprises periodically introducing additional oxidizing agent into the body of water to replenish the content therein of biocidal species.

Yet another embodiment of this invention provides a composition which comprises a solid mixture of (i) a water soluble dialkylhydantoin wherein the alkyl groups are the same or different and each alkyl group contains 1 to about 6 carbon atoms, and (ii) a source of bromide ion, wherein the molar ratio of water soluble dialkylhydantoin to source of bromide ion in the mixture is in the range of about 1.2:1 to about 7.2:1.

A non-exhaustive list of bodies of water that may be sanitized using this invention includes cooling water systems, pasteurizing systems, waste water effluents, pulp and paper mills, swimming pools, hot tubs, spas, fountains, water attractions, oil fields, air washers, fire reservoirs, and evaporative condensers. Organisms which are destroyed by the practice of this invention include, for example, bacteria, fungi, algae, slime, and mollusks.

Further embodiments of this invention will become apparent from the following detailed description and appended claims.

DETAILED DESCRIPTION OF THE INVENTION

It will now be appreciated that this invention provides, among other things, for the in situ generation of biocidal species for water sanitization. This is accomplished by the addition of a dialkylhydantoin and a source of bromide ion, both at low concentration, to the body of water, in which at least a portion of the body of water is contacted with an oxidizing agent; this system is stable for weeks. It has been found that using lower concentrations of bromide ion than are taught in the prior art yields desirable levels of biocidal activity. Further, it has been observed that the presence of a dialkylhydantoin inhibits the irreversible formation of bromate ion, a possible carcinogen.

In the present invention, the alkyl groups of the dialkylhydantoin may be the same or different, and are both bound to the carbon atom at the 5-position of the hydantoin ring. Suitable alkyl groups include methyl, ethyl, isopropyl, tert-butyl, methylcyclopentyl, cyclohexyl, and the like. Preferred

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alkyl groups are ethyl and methyl; preferred dialkylhydantoins are 5-ethyl-5-methyl-hydantoin and 5,5-dimethylhydantoin; 5,5-dimethylhydantoin is highly preferred as the dialkylhydantoin moiety. It is desired that the concentration of the added dialkylhydantoin is in the range of from about 0.15 to about 0.70 millimole per liter; the concentration of dialkylhydantoin preferably is in the range of from about 0.50 millimole per liter to about 0.62 millimole per liter.

Bromide ions may be obtained from any convenient source; the source is preferably a solid, and nonhazardous to humans. It is preferred to use water soluble metal bromide salts or water soluble ammonium bromide salts. Examples of water soluble metal bromide salts that may be used include sodium bromide, potassium bromide, magnesium bromide, calcium bromide, and zinc bromide. Tetraethylammonium bromide, tetramethylammonium bromide, and ammonium bromide are examples of water soluble ammonium bromide salts that may be used in the practice of this invention. Sodium bromide is the most highly preferred source of bromide ion. The desired concentration of the source of bromide ion is in the range of from about 0.090 to about 0.39 millimole per liter, with the preferred concentration in the range of from about 0.20 millimole per liter to about 0.35 millimole per liter. Although the source of bromide ion concentration is much lower than previously reported, it is enough to maintain an available halogen concentration of from about 0.5 to about 8 milligrams per liter, expressed as Br_2, which is sufficient to keep the body of water sanitary.

The molar ratio of added dialkylhydantoin to added source of bromide ion is typically in the range of from about 1.2:1 to about 7.2:1; a preferred molar ratio is in a range from about 1.5:1 to about 3.2:1.

A wide variety of oxidizing agents may be used, including alkali metal monopersulfates such as potassium monopersulfate, alkali metal peroxides, and chlorine sources; however, the oxidizing agent is preferably a chlorine source. Chlorine sources include Cl_2, hypochlorite ions, and hypochlorous acid. More preferably, the chlorine source is a source of hypochlorite ion or hypochlorous acid. Examples of sources of hypochlorite ion and hypochlorous acid include sodium hypochlorite, lithium hypochlorite, calcium hypochlorite, trichloroisocyanuric acid, and sodium dichloroisocyanurate. Preferred hypochlorous acid or hypochlorite ion sources include trichloroisocyanuric acid, sodium dichloroisocyanurate, and calcium hypochlorite, all most preferably in solid form; a highly preferred oxidizing agent is solid trichloroisocyanuric acid.

Contact of the source of bromide ion with the oxidizing agent in the presence of a dialkylhydantoin results in the formation of monohalogenated hydantoins. The monohalogenated hydantoins may act as biocidal agents themselves, or they may store biocidal bromine. For example, hydrolysis of halogenated hydantoins is known to produce hypobromous acid, a well-known biocide. An advantage of this invention is that the monohalohydantoins produced are predominately bromohydantoins; it is well-known that bromoamines are much less irritating to human mucous membranes than are chloroamines, which is particularly useful in certain applications, such as swimming pools. A further advantage of this invention is the inhibition of the formation of bromate ions, a very desirable feature, due to the suspected toxicity of bromate ions, and also because bromate ion formation irreversibly consumes bromide ions.

It is desirable to employ a solid mixture of a dialkylhydantoin and a source of bromide ion. This is especially true

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when convenient handling is a priority, since sources of bromide ion, especially water soluble bromide salts, may be very deliquescent. Once a hygroscopic salt has absorbed enough moisture, particles of the solid clump together so that it is no longer free-flowing, making it difficult to handle and dose properly to the body of water in need of sanitization. Thus, the use of a solid mixture of dialkylhydantoin and source of bromide ion is advantageous: the mixture is much less deliquescent than that of the unmixed source of bromide ion, and also provides a constant ratio of dialkylhydantoin to source of bromide ion. The constant ratio of dialkylhydantoin to source of bromide ion further simplifies handling errors by the user of the solid mixture.

The dialkylhydantoin and source of bromide ion may be added directly to the body of water as solids or either or both may be predissolved in a separate vessel and then added to the body of water. The dialkylhydantoin and source of bromide ion, regardless of form, are added to the body of water needing sanitization simultaneously or in any order. Direct addition of both the dialkylhydantoin and source of bromide ion to the body of water as solids is preferred. When a solid mixture of dialkylhydantoin and source of bromide ion is used, it may be added to the body of water needing sanitization or predissolved in a separate vessel and then added to the body of water. It is preferred to add the solid mixture directly to the body of water.

The oxidizing agent may be added in one or more ways, depending on the setup of the particular system. Adding the oxidant directly to the main body of water is feasible. In systems in which the water is circulated through an apparatus, the oxidant may be added to this apparatus. Highly preferred is the addition of the oxidant to an apparatus through which the water circulates.

Although the dialkylhydantoin and source of bromide ion are regenerated, performing biocidal functions does consume oxidizing agent. In order to maintain about 0.5 to about 8 milligrams per liter of available halogen, expressed as Br_2, the oxidant must be replenished periodically (e.g., twice a week). In reality, physical and chemical losses of dialkylhydantoin and source of bromide ion do occur, so they also need occasional replenishment (e.g., once every two weeks). Physical loss pathways for dialkylhydantoins and sources of bromide ion are described in detail in U.S. Pat. No. 5,662,940.

In a highly preferred embodiment, solid sodium bromide and solid dimethylhydantoin are dissolved in the body of water under conditions of very high dilution. A portion of the water is allowed to contact trichloroisocyanuric acid, which produces hypochlorous acid and/or hypochlorite ion, which in turn produces biocidal species in situ upon contact with bromide ions.

In another highly preferred embodiment, the solid mixture of sodium bromide and dimethylhydantoin is dissolved in the body of water under conditions of very high dilution. A portion of the water is allowed to contact trichloroisocyanuric acid, which produces hypochlorous acid and/or hypochlorite ion, which in turn produces biocidal species in situ upon contact with bromide ions.

In still another highly preferred embodiment of this invention, solid sodium bromide and solid dimethylhydantoin are dissolved under conditions of high dilution in a body of water which has conditions corresponding to chlorine lock. The high concentrations of cyanuric acid and chloride ion that characterize chlorine lock do not affect the ability of bromine biocidal species to sanitize the body of water. A portion of the water is allowed to contact trichloroisocya-

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nuric acid, which produces hypochlorous acid and/or
hypochlorite ion, which in turn produces biocidal species in
situ upon contact with bromide ions. This thus allows
sanitization of the "chlorine-locked" body of water while
alleviating the need for draining the body of water.

The following examples are presented for purposes of
illustration, and are not intended to impose limitations on the
scope of this invention. Examples 1, 2, and 3 demonstrate
that dimethylhydantoin stabilization of bromine biocidal
species is viable for several weeks. Examples 2 and 3 further
demonstrate the presence of monohalohydantoins in the pool
water. Example 4 shows the correlation between the loss of
dimethylhydantoin and the appearance of bromate ion.
Examples 5 and 6 simulate the conditions of chlorine lock,
and demonstrate, via the oxidation-reduction potential data,
that bromine biocides are effective water sanitizers under
such conditions. Examples 4 and 5 also show, via the
available bromine measurement, that a lesser amount of
bromide ion relative to dimethylhydantoin still provides
enough available halogen for biocidal activity.

EXAMPLE 1

Pool A, an above-ground, vinyl-lined swimming pool
with a volume of 12,300 gallons, was used in this experi-
ment The water was recirculated with a 1 HP pump through
a high rate sand filter on a 12-hour cycle (on at 7:00 am, off
at 7:00 pm). Pool A was known to already contain NaBr, so,
in the interest of saving water, the concentration was
adjusted to 50 ppm by addition of the appropriate amount of
solid NaBr. The pool was dosed with 40 ppm dimethylhy-
dantoin by broadcasting the solid to the water. On the
suction side of the pump, a portion of the water was diverted
through a dedicated calcium hypochlorite feeder, charged
with 3", 10 oz. calcium hypochlorite tablets manufactured
by PPG Industries. This water was then routed immediately
to the bulk pool water. The feeder control valve was adjusted
to maintain a residual of 1–2 mg/L total available chlorine,
as measured by the diethylphenyldiamine (DPD) colorimet-
ric method. Measurements were made at 1:00 pm daily, and
adjustments to the feeder were made accordingly. When
necessary, calcium hypochlorite was replenished. Table 1
lists the amount of calcium hypochlorite consumed during a
three week period; the total amount of calcium hypochlorite
used was 12.5 pounds. The high rate of consumption in the
early phases of the test might be attributed to a high organic
load, as the pool was recovering from an algal bloom.
Nevertheless, when the test was terminated, the pool water
was clear and algae-free.

In Examples 2 and 3, a short reverse phase liquid chro-
matography (LC) guard column was used in the analyses.
Initial experiments showed that 1-chloro-3-bromo-5,5-
dimethylhydantoin is retained on the LC column when water
is the mobile phase. The 1 -chloro-3-bromo-5,5-dimethyl-
hydantoin eluted when the mobile phase was switched to
acetonitrile/water. Although as little as 5% acetonitrile/water
may be used, for these analyses 20% acetonitrile/water was
used as the mobile phase.

A Finnigan TSQ 7000 mass spectrometer with an Atmo-
spheric Pressure Chemical Ionization interface was used for
liquid chromatography/mass spectroscopy (LC/MS). To
confirm that 1-chloro-3-bromo-5,5-dimethylhydantoin
could be detected in this analysis, the negative ion mass
spectrum was obtained using acetonitrile and acetonitrile/
water loop injections. The spectrum showed the parent
ion-H cluster (M-Br-Cl) centered on m/z 241. In the nega-
tive ion mass spectral mode, 1 mg/L 1-chloro-3-bromo-5,5-

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dimethylhydantoin (10 μL injection) can be detected. The
monobromohydantoin (M-Br; m/z=161,163), monochloro-
hydantoin (M-Cl; m/z=205,207), Cl (m/z=35,37), and Br
(m/z=79,81) isotopic anions were observed. The M-Br and
M-Cl ions were monitored for LC/MS analysis.

The same procedure was used for the 1 ppm 1-chloro-3-
bromo-5,5-dimethylhydantoin standard and the samples.
After the sample was introduced to the LC column, an
excess of the water mobile phase was pumped through the
LC column to remove water soluble compounds such as
dimethylhydantoin. Next, the mobile phase was changed to
20% acetonitrile/water in order to elute the halodimethyl-
hydantoins. For greater sensitivity in detecting the halodim-
ethylhydantoin moieties from the pool samples, the LC
sample size was increased to 100 μL (5×20 μL injections).

EXAMPLE 2

The chemical treatment program of Pool A (described in
Example 1) was changed. The calcium hypochlorite was
removed from the feeder, and the control valve was closed;
the water was not changed. Trichloroisocyanuric acid in the
form of 3", 8 oz. tablets was placed in the pool skimmer
basket. The number of tablets was adjusted to maintain a
residual of 1–2 mg/L total available chlorine as measured by
the diethylphenyldiamine (DPD) colorimetric method. Mea-
surements were made at 1:00 pm daily, and adjustments
were made accordingly. When necessary, trichloroisocyanu-
ric acid was replenished. Table 1 lists the amount of trichlor-
oisocyanuric acid consumed during a four week period. It
can be seen that the consumption of trichloroisocyanuric
acid remains fairly constant throughout the test period.
Furthermore, the water remained clear and algae-free.

Samples of water from Pool A were removed from the
pool at initial phases of the experiment and immediately
analyzed by LC/MS. The LC/MS analyses show peaks at
m/z=161 and 163 as well as m/z=205 and 207; therefore,
monohalodimethylhydantoin compounds are present in the
pool water samples. The concentration of halogenated
hydantoins for Pool A was 1.8 mg/L, mostly as
monobromohydantoin, based on a comparison with an exter-
nal standard solution of 1-chloro-3-bromo-5,5-
dimethylhydantoin.

EXAMPLE 3

A slightly different treatment program was performed on
an adjacent pool, Pool B. This was an above-ground, vinyl-
lined swimming pool with a volume of 12,300 gallons. The
water was recirculated with a 1 HP pump through a high rate
sand filter, on a 12 hour cycle (on at 7:00 am, off at 7:00 pm).
Pool B was known to already contain NaBr, so, in the
interest of saving water, the concentration was adjusted to 50
ppm by addition of the appropriate amount of solid NaBr.
The pool was dosed with 40 ppm dimethylhydantoin by
broadcasting the solid to the water. On the discharge side of
the pump after the filter, a portion of the water was diverted
through a dedicated trichloroisocyanuric acid feeder charged
with 3" tablets. This water was then routed immediately to
the bulk pool water. The feeder control valve was adjusted
to maintain a residual of 1–2 mg/L total available chlorine
as measured by the diethylphenyldiamine (DPD) colorimet-
ric method. Measurements were made at 1:00 pm daily, and
adjustments to the feeder were made accordingly. When
necessary, 3" trichloroisocyanuric acid tablets were replen-
ished. Table 1 lists the amount of trichloroisocyanuric acid
consumed during an eight week period; the average amount
of trichloroisocyanuric acid consumed was 1.8 pounds per
week.

Samples of water from Pool B were removed from the pool at initial phases of the experiment and immediately analyzed by LC/MS. The LC/MS analyses show peaks at mz=161 and 163 as well as m/z=205 and 207; therefore, monohalodimethylhydantoin compounds are present in the pool water samples. The concentration of halogenated hydantoins for Pool B was 4.1 mg/L, mostly as monobromohydantoin, based on a comparison with an external standard solution of 1-chloro-3-bromo-5,5-dimethylhydantoin.

TABLE 1

week #	Example 1 $Ca(OCl)_2$, lbs.	Example 2 trichloroisocyanuric acid, lbs.	Example 3 trichloroisocyanuric acid, lbs.
1	5.3	2.6	1.6
2	4.5	2.2	2.2
3	2.7	2.6	1.3
4	—	2.6	0.4
5	—	—	2.2
6	—	—	1.8
7	—	—	1.3
8	—	—	0.9

EXAMPLE 4

Three pools, Pools 1, 2, and 3, were monitored for this experiment; all three pools are in-ground swimming pools with a volume of 20,000 gallons. Every two weeks, each pool was dosed with 12 ppm NaBr and 12 ppm dimethylhydantoin by broadcasting the solids to the water. In all three pools, the oxidant used was trichloroisocyanuric acid. In Pools 1 and 2, the trichloroisocyanuric acid was administered via the skimmer basket; in Pool 3, the trichloroisocyanuric acid was administered via a feeder. A residual of 1–3 mg/L total available chlorine was maintained, as measured by the diethylphenyldiamine (DPD) colorimetric method. Measurements of the available chlorine were made weekly. When necessary, trichloroisocyanuric acid was replenished.

Samples of water were removed from each pool approximately once a week and analyzed. Dimethylhydantoin was monitored by HPLC, while bromate ion and bromide ion were monitored by ion chromatography. Table 2 shows the approximate amounts of dimethylhydantoin, bromate ion, and bromide ion, in parts per million, for each of the three pools.

TABLE 2

Pool 1	day	1	6	10	18	26	29	36	42	50	57	64	71		73	85
	DMH[a]	44	43	37	30	32	29	29	24	17	14	8	0		27[b]	17
	bromate	0	0	0	0	0	0	0	0	0	1	5			6	6
	bromide	50	35	30	31	34	33	33	32	33	29	30	26		28	23
Pool 2	day	1	6	10	18	23	30	36	42	50	57	64	71		78	85
	DMH[a]	33	27	30	29	19	20	14	13	8	3	4	0		26[b]	28
	bromate	0	0	0	0	0	0	0	0	0	0	1	7		8	15
	bromide	38	20	23	26	29	39	28	36	26	42	27	20		21	20
Pool 3	day	1	—	10	18	22	30	39	43	50	57	—	—		74	85
	DMH[a]	52	—	43	33	20	23	7	0	4	0	—	—		2	5[b]
	bromate	0	—	0	0	0	6	5	5	7	—	—			13	12
	bromide	36	—	27	34	27	36	20	14	18	15	—	—		7	9

[a]DMH = dimethylhydantoin
[b]more dimethylhydantoin added to pool

EXAMPLE 5

Five vessels, each containing 1000 mL of water, had cyanuric acid added to them to yield concentrations of

7.75×10^{-5}, 1.55×10^{-4}, 3.88×10^{-4}, 7.75×10^{-4}, and 3.88×10^{-3} M, respectively. A sixth vessel, also containing 1000 mL of water, did not have any cyanuric acid added. The oxidation-reduction potential of all six solutions was measured using a platinum wire electrode, with Ag/Ag$^+$ as a reference electrode. Enough NaBr was added to each vessel to yield a concentration of 1.94×10^{-4} M; sodium hypochlorite was added to oxidize the bromide ions. After 5 minutes, another measurement of the oxidation-reduction potential of each solution was then removed, and the available bromine concentration of each solution was determined by iodometric titration with platinum triode. The oxidation-reduction potential in millivolts is shown in Table 2 for each solution, along with the available bromine concentration in ppm.

TABLE 3

				(Example 5)		
cyanuric acid concentration, M	0	7.75×10^{-5}	1.55×10^{-4}	3.88×10^{-4}	7.75×10^{-4}	3.88×10^{-3}
initial potential, mV	726.0	691.5	682.0	658.7	660.0	631.6
potential with NaBr, mV	766.6	773.0	772.3	764.3	752.4	714.2
available Br$_2$, ppm	3.4	3.5	3.4	3.7	3.4	3.4

EXAMPLE 6

Five vessels, each containing 1000 mL of water, had cyanuric acid added to them to yield concentrations of 7.75×10^{-5}, 1.55×10^{-4}, 3.88×10^{-4}, 7.75×10^{-4}, and 3.88×10^{-3} M, respectively. A sixth vessel, also containing 1000 mL of water, did not have any cyanuric acid added. The oxidation-reduction potential of all six solutions was measured using a platinum wire electrode, with Ag/Ag$^+$ as a reference electrode. Enough of a 30:70 (wt.) NaBr:dimethylhydantoin solid blend was added to each solution to yield a concentration of 30 ppm of blend (8.74×10^{-5} M NaBr; 1.64×10^{-4} M dimethylhydantoin); sodium hypochlorite was added to oxidize the bromide ions. After 5 minutes, another measurement of the oxidation-reduction potential of each solution was recorded. More of the 30:70 (wt.) NaBr:dimethylhydantoin blend was added to each vessel such that the total concentration of blend was 60 ppm (1.75×10^{-4} M NaBr; 3.28×10^{-4} M dimethylhydantoin). Sodium hypochlorite was again added to oxidize the bromide ions. After 5 minutes, the oxidation-reduction potential of all six solutions was again measured. A 20 mL aliquot of each solution was then removed, and the available bromine concentration

of each solution was determined by iodometric titration with platinum triode. Table 3 shows the oxidation-reduction potential in millivolts for each solution, as well as the available bromine concentration in ppm.

6 carbon atoms, and in the range of about 0.090 to about 0.38 millimole per liter of a water soluble source of bromide ion selected from the group consisting of metal bromide salts and ammonium bromide salts, and providing to said body of

TABLE 4

(Example 6)

cyanuric acid concentration, M	0	7.75×10^{-5}	1.55×10^{-4}	3.88×10^{-4}	7.75×10^{-4}	3.88×10^{-3}
initial potential, mV	720.9	685.4	678.8	667.7	657.6	619.6
potential with blend* (30 ppm), mV	625.5	641.9	647.6	647.2	646.6	623.0
potential with blend* (60 ppm), mV	591.2	611.7	615.0	623.6	618.2	600.9
available Br₂, ppm	1.6	1.6	1.6	1.6	1.6	1.1

*30:70 (wt.) NaBr₂dimethylhydantoin blend

It is to be understood that the reactants and components referred to by chemical name or formula anywhere in the specification or claims hereof, whether referred to in the singular or plural, are identified as they exist prior to coming into contact with another substance referred to by chemical name or chemical type (e.g., another reactant, a solvent, or etc.). It matters not what preliminary chemical changes, transformations and/or reactions, if any, take place in the resulting mixture or solution or reaction medium as such changes, transformations and/or reactions are the natural result of bringing the specified reactants and/or components together under the conditions called for pursuant to this disclosure. Thus the reactants and components are identified as ingredients to be brought together in connection with performing a desired chemical reaction or in forming a mixture to be used in conducting a desired reaction. Accordingly, even though the claims hereinafter may refer to substances, components and/or ingredients in the present tense ("comprises", "is", etc.), the reference is to the substance, component or ingredient as it existed at the time just before it was first contacted, blended or mixed with one or more other substances, components and/or ingredients in accordance with the present disclosure. Whatever transformations, if any, that occur in situ as the catalytic reaction is conducted is what the claim is intended to cover. Thus the fact that a substance, component or ingredient may have lost its original identity through a chemical reaction or transformation during the course of contacting, blending or mixing operations, if conducted in accordance with this disclosure and with the application of common sense and the ordinary skill of a chemist, is thus wholly immaterial for an accurate understanding and appreciation of the true meaning and substance of this disclosure and the claims thereof.

Each and every patent or other publication referred to in any portion of this specification is incorporated in toto into this disclosure by reference, as if fully set forth herein.

This invention is susceptible to considerable variation in its practice. Therefore the foregoing description is not intended to limit, and should not be construed as limiting, the invention to the particular exemplifications presented hereinabove. Rather, what is intended to be covered is as set forth in the ensuing claims and the equivalents thereof permitted as a matter of law.

What is claimed is:

1. A method of sanitizing a body of water, which method comprises introducing into said body of water in the range of about 0.26 to about 0.70 millimole per liter of a water soluble dialkylhydantoin wherein the alkyl groups are the same or different and each alkyl group contains 1 to about

water an amount of an oxidizing agent capable of oxidizing bromide ion in situ.

2. A method according to claim 1 wherein said dialkyl-hydantoin is 5,5-dimethylhydantoin or 5-ethyl-5-methylhydantoin.

3. A method according to claim 1 wherein said source of bromide ion is a water soluble metal bromide salt or water soluble ammonium bromide salt.

4. A method according to claim 3 wherein said source of bromide ion is sodium bromide.

5. A method according to claim 1 wherein the source of bromide ion and the dialkylhydantoin are added as a solid mixture.

6. A method according to claim 5 wherein the molar ratio of dialkylhydantoin to source of bromide ion is from about 1.2:1 to about 7.2:1.

7. A method according to claim 1 wherein said oxidizing agent is a chlorine source.

8. A method according to claim 7 wherein said chlorine source is selected from the group consisting of a water soluble hypochlorite salt, trichloroisocyanuric acid, or a water soluble salt of trichloroisocyanuric acid.

9. A method according to claim 1 wherein the addition of said dialkylhydantoin, said source of bromide ion and said oxidizing agent to said body of water yields in the range of about 0.5 to about 8 milligrams per liter of total available halogen, expressed as Br₂.

10. A method according to claim 1 wherein said body of water is an outdoor swimming pool.

11. A method of sanitizing a body of water, which method comprises introducing into said body of water ingredients comprising:

   (i) a composition which comprises a solid mixture of (a) a water soluble dialkylhydantoin wherein the alkyl groups are the same or different and each alkyl group contains 1 to about 6 carbon atoms, and (b) a source of bromide ion selected from the group consisting of water soluble metal bromide salts and water soluble ammonium bromide salts, wherein the molar ratio of water soluble dialkylhydantoin to source of bromide ion in the mixture ranges from about 1.2:1 to about 7.2:1, and

   (ii) an oxidizing agent;

the amount of said dialkylhydantoin introduced into said body of water being in the range of from about 0.26 to about 0.70 millimole per liter of water.

12. A method according to claim 11 wherein the source of bromide ion is a water soluble metal bromide salt or water soluble ammonium bromide salt.

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13. A method according to claim 11 wherein at least (i) is introduced in undissolved form into said body of water.

14. A method according to claim 11 wherein said dialkylhydantoin is 5,5-dimethylhydantoin and said source of bromide ion is sodium bromide.

15. A method according to claim 11 wherein said oxidizing agent is a chlorine source.

16. A method according to claim 15 wherein said chlorine source is selected from the group consisting of a water soluble hypochlorite salt, trichloroisocyanuric acid, or a water soluble salt of trichloroisocyanuric acid.

17. A method according to claim 16 wherein said chlorine source is trichloroisocyanuric acid.

18. A method according to claim 11 wherein the addition of (i) and (ii) to said body of water yields in the range of about 0.5 to about 8 milligrams per liter of total available halogen, expressed as Br_2.

19. A method according to claim 11 wherein said dialkylhydantoin is 5,5-dimethylhydantoin, wherein said source of bromide ion is sodium bromide, wherein said oxidizing agent is a chlorine source, and wherein the addition of (i) and (ii) to said body of water yields in the range of about 0.5 to about 8 milligrams per liter of total available halogen, expressed as Br_2.

20. A method according to claim 11 wherein said water soluble dialkylhydantoin is 5,5-dimethylhydantoin or 5-ethyl-5-methylhydantoin.

21. A method according to claim 11 wherein said amount of dialkylhydantoin is in the range of from about 0.50 to about 0.62 millimole per liter of water.

22. A method according to claim 21 wherein the addition of (i) and (ii) to said body of water yields in the range of about 0.5 to about 8 milligrams per liter of total available halogen, expressed as Br_2.

23. A method according to claim 11 wherein said body of water is an outdoor swimming pool.

24. A method of sanitizing a body of water, which method comprises:

a) introducing into said body of water (i) a composition which comprises a granular mixture of (A) a water soluble dialkylhydantoin wherein the alkyl groups are the same or different and each alkyl group contains 1 to about 6 carbon atoms, and (B) a source of bromide ion selected from the group consisting of water soluble metal bromide salts and water soluble ammonium bromide salts, wherein the molar ratio of water soluble dialkylhydantoin to source of bromide ion in the mixture ranges from about 1.2:1 to about 7.2:1, and (ii) an oxidizing agent, the amount of said dialkylhydantoin introduced into said body of water being in the rant of from about 0.26 to about 0.70 millimole per liter of water, and

b) periodically introducing additional oxidizing agent into said body of water.

25. A method according to claim 24 wherein said oxidizing agent is a chlorine source.

26. A method according to claim 24 wherein said chlorine source is selected from the group consisting of a water soluble hypochlorite salt, trichloroisocyanuric acid, or a water soluble salt of trichloroisocyanuric acid.

27. A method according to claim 26 wherein said chlorine source is trichloroisocyanuric acid.

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28. A method according to claim 24 wherein said water soluble dialkylhydantoin is 5,5-dimethylhydantoin, said source of bromide ion is sodium bromide, and wherein said oxidizing agent is a chlorine source.

29. A method according to claim 24 wherein the addition of (i) and (ii) to said body of water yields in the range of about 0.5 to about 8 milligrams per liter of total available halogen, expressed as Br_2.

30. A method according to claim 24 wherein said dialkylhydantoin is 5,5-dimethylhydantoin, wherein said source of bromide ion is sodium bromide, wherein said oxidizing agent is a chlorine source, and wherein the addition of (i) and (ii) to said body of water yields in the range of about 0.5 to about 8 milligrams per liter of total available halogen, expressed as Br_2.

31. A method according to claim 24 wherein the oxidizing agent is introduced into said body of water as required, such that in the range of about 0.5 to about 8 milligrams per liter of total available halogen, expressed as Br_2, is maintained within said body of water.

32. A method according to claim 24 wherein said water soluble dialkylhydantoin is 5,5-dimethylhydantoin or 5-ethyl-5-methylhydantoin.

33. A method according to 32 claim wherein said dialkylhydantoin is 5,5-dimethylhydantoin and said source of bromide ion is sodium bromide.

34. A method according to claim 24 wherein the source of bromide ion is a water soluble metal bromide salt or a water soluble ammonium bromide salt.

35. A method according to claim 24 wherein said amount of dialkylhydantoin is in the range of from about 0.50 to about 0.62 millimole per liter of water.

36. A method according to claim 35 wherein the addition of (i) and (ii) to said body of water yields in the range of about 0.5 to about 8 milligrams per liter of total available halogen, expressed as Br_2.

37. A method according to claim 24 wherein said body of water is an outdoor swimming pool.

38. A method according to claim 24 wherein at least (i) is introduced in undissolved form into said body of water.

39. A method of sanitizing a body of water, which method comprises introducing into said body of water in the range of from about 0.50 to about 0.62 millimole per liter of a water soluble dialkylhydantoin wherein the alkyl groups are the same or different and each alkyl group contains 1 to about 6 carbon atoms, and in the range of about 0.090 to about 0.38 millimole per liter of a water soluble source of bromide ion selected from the group consisting of metal bromide salts and ammonium bromide salts, and providing to said body of water an amount of an oxidizing agent capable of oxidizing bromide ion in situ.

40. A method according to claim 39 wherein said body of water is an outdoor swimming pool.

41. A method according to claim 39 wherein the molar ratio of water soluble dialkylhydantoin to source of bromide ion is from about 1.2:1 to about 7.2:1.

42. A method according to claim 11 wherein the introduction of said water soluble dialkylhydantoin and said source of bromide ion into said body of water yields in the range of about 0.5 to about 8 milligrams per liter of total available halogen, expressed as Br_2.

*   *   *   *   *

(12) **REEXAMINATION CERTIFICATE** (4779th)

United States Patent
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(45) **Certificate Issued:** May 13, 2003

(54) **SOLID MIXTURES OF DIALKYLHYDANTOINS AND BROMIDE ION SOURCES FOR WATER CONTAMINATION**

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Primary Examiner—Peter A. Hruskoci

(57) **ABSTRACT**

A water soluble dialkylhydantoin and a source of bromide ion are added to a body of water needing sanitization. This is followed by contacting the body of water with an oxidizing agent, which creates biocidal species in situ in the body of water.

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REEXAMINATION CERTIFICATE ISSUED UNDER 35 U.S.C. 307

NO AMENDMENTS HAVE BEEN MADE TO
THE PATENT

2

AS A RESULT OF REEXAMINATION, IT HAS BEEN
DETERMINED THAT:

The patentability of claims 1–42 is confirmed.

* * * * *

In re Patent Application of:
Michael Ludensky et al.

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Examiner: P. A. Hruskoci

DECLARATION OF PHILIP G. SWEENY, PH.D. UNDER 37 C.F.R. § 1.132

Exhibit D

US006641828B1

(54) **METHODS FOR MICROBIOLOGICAL CONTROL IN AQUEOUS SYSTEMS**

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(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 33 days.

This patent is subject to a terminal disclaimer.

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(57) **ABSTRACT**

Microbiological control in aqueous media and/or eradication or reduction of biofilm on a surface in contact with such media is achieved by introducing into the aqueous medium a microbiocidally effective quantity of one or more 1,3-dibromo-5,5-dialkylhydantoins where one of the alkyls is methyl and the other is a C_{1-4} alkyl, wherein (i) the molar quantity of 1,3-dibromo-5,5-dialkylhydantoin introduced is less than the molar quantity of N,N'-bromochloro-5,5-dimethylhydantoin that would be required to effect the same degree of microbiological control in that medium, (ii) the molar quantity of the 1,3-dibromo-5,5-dialkylhydantoin introduced releases an amount of "free chlorine" that is greater than the amount of "free chlorine" that would be released in that medium by an equimolar quantity of N,N'-bromochloro-5,5-dimethylhydantoin, and (iii) the amount of "free chlorine" released by the quantity of the 1,3-dibromo-5,5-dialkylhydantoin introduced is greater than the amount of "free chlorine" that could be predicted to be released by that quantity of 1,3-dibromo-5,5-dialkylhydantoin on the basis of the amount of "free chlorine" that would be released in that medium by an equimolar quantity of N,N'-bromochloro-5,5-dimethylhydantoin.

27 Claims, 2 Drawing Sheets

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BCDMH Vs DBDMH
Relative Distribution of Free & Total Cl
Simulated Cooling Water: pH 9.1, Temp 100 F, CH = 400 ppm, TA = 300 ppm

Legend:
- Free Cl (BCDMH)
- Free Cl (DBDMH)
- Total Cl (DBDMH)
- Total Cl (BCDMH)
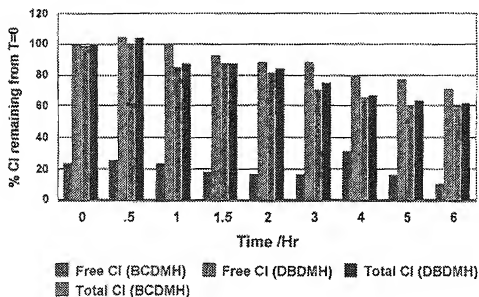
Fig. 1

BCDMH Vs DBDMH
% Hydrolysis to "Free Chlorine"
Simulated Cooling Water: pH 9.1, Temp 100 F, CH = 400 ppm, TA = 300 ppm
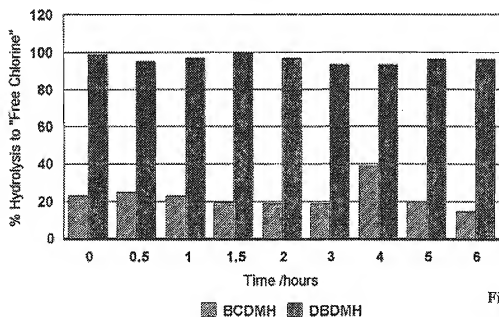
Fig. 2

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METHODS FOR MICROBIOLOGICAL CONTROL IN AQUEOUS SYSTEMS

REFERENCE TO RELATED APPLICATION

This is a continuation-in-part of commonly-owned copending application Ser. No. 09/484,938, filed Jan. 18, 2000.

REFERENCE TO OTHER COMMONLY-OWNED APPLICATIONS

Commonly-owned copending application Ser. No. 09/484,844, filed Jan. 18, 2000, describes and claims chemical processes from which compositions of the present invention can be formed or derived. Commonly-owned copending application Ser. No. 09/484,687, filed Jan. 18, 2000, describes and claims 1,3-dibromo-5,5-dimethylhydantoin particulate solids producible by the processes of application Ser. No. 09/484,844, such solids having unprecedented enhanced properties, and compacted articles made from such particulate solids without use of a binder. Commonly-owned copending application Ser. No. 09/487,816, filed Jan. 18, 2000, relates in part to converting 1,3-dihalo-5,5-dimethylhydantoins into compacted articles using novel binders. Commonly-owned copending application Ser. No. 09/484,891, filed Jan. 18, 2000, relates to the compacting of 1,3-dihalo-5,5-dimethylhydantoins other than 1,3-dibromo-5,5-dimethylhydantoin without use of binders, and to the novel compacted forms so produced. Commonly-owned copending application Ser. No. 09/483,896, filed Jan. 18, 2000, relates to the granulation of small average particle size 1,3-dibromo-5,5-dimethylhydantoin and also to the compaction of such granulated products to form larger-sized articles.

BACKGROUND

As is known in the art of water treatment for microbiological control, a deficiency of chlorine, of hypochlorites, and of certain halogenated organic water-treating agents is the formation, during usage, of undesirable disinfection by-products. These by-products are undesirable both from the standpoint of environmental concerns and also from the standpoint of toxicological considerations.

Certain 1,3-dihalo-5,5-dialkylhydantoins have been found to be effective as biocides for aqueous systems such as industrial cooling water, recreational water, and wastewater.

Persons using biocidal agents in the biocidal treatment of water customarily, if not universally, refer to "free chlorine" level as a measure of biocidal control. To achieve "free chlorine" levels in water treatment, solid materials are often preferred because of their high weight percent activity. N,N'-bromochloro-5,5-dimethylhydantoin (BCDMH) has been one of the most widely-used solid sources of "free chlorine" for water treatment. One of the features emphasized for BCDMH by suppliers of BCDMH is that in use, the combined chlorine from the biocide regenerates "free chlorine" by reaction with inactive bromide species formed during the water treatment operation. In other words, the chlorine atom in the initial N,N'-bromochloro-5,5-dialkylhydantoin is said to be a precursor for additional "free chlorine" for sanitation purposes.

In use, BCDMH hydrolyzes into HOBr and HOCl both of which register as "free chlorine" species in commonly-used standard test procedures. These methods for determining "free chlorine" levels in treated water, involve use of a

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reagent known as DPD (i.e., N,N'-diethyldiphenylenediamine) and a buffer, and the results of such analyses are commonly used, if not universally used, as the basis for determining the quantity of a halogen-containing microbiocidal agent to be used for water treatment. Heretofore, consumers of BCDMH have only been concerned with the level of "free chlorine" provided by a given quantity of that biocidal material. What has not been realized by such consumers is the amount of "total chlorine" being utilized in order to achieve the requisite "free chlorine" level. As a consequence, the consumer has not had available a yardstick by which to determine the true economic efficiency of using BCDMH as a biocidal agent in the treatment of water. To achieve optimum economic efficiency, the consumer should have available for use a biocidal agent in which the amount of "free chlorine" released into the water corresponds closely to the "total chlorine" content of the biocidal agent.

In the event a biocidal agent provides a relatively small amount of "free chlorine" in relation to its "total chlorine" content, it has been deemed necessary to utilize a relatively large amount of such agent in order to achieve microbiological control. This in turn means high levels of halogenated materials are released into the environment. If on the other hand, a biocidal agent could provide to the water an amount of "free chlorine" that closely corresponds to the "total chlorine" content of the biocidal agent, effective microbiological control could be realized by use of much smaller dosages and with consequent minimal adverse impact upon the environment.

BRIEF SUMMARY OF THE INVENTION

This invention involves, inter alia, the discovery that there is a substantial disparity between the "free chlorine" level and the "total chlorine" level delivered to the water when using BCDMH as a biocidal agent. Thus the consumer of BCDMH as a water treating agent unknowingly has been paying for a relatively ineffective microbiocidal agent. Moreover, such consumer has been contributing unknowingly to the release of undesirable quantities of halogenated materials to the environment.

This invention further involves, inter alia, the discovery that the level of "free chlorine" available from 1,3-dibromo-5,5-dimethylhydantoin (DBDMH), especially when used in water having a pH of at least about 8.0, closely approximates its "total chlorine" content. Consequently the use of one or more water-soluble dialkyldibromohydantoins such as DBDMH as a water treating agent, especially when used in the treatment of industrial cooling water, is highly effective from an economic standpoint and highly desirable from an environmental standpoint. That is to say, the dosage levels of water-soluble dialkyldibromohydantoins such as DBDMH needed to provide effective microbiological control with respect to such undesirable organisms and pathogens as bacteria, algae, and biofilms, are relatively low compared to dosage levels of BCDMH required for the same degree of control, especially in industrial cooling water. Moreover, the levels of halogenated materials released to the environment are much smaller when using a water-soluble dialkyldibromohydantoin such as DBDMH as compared to BCDMH.

Accordingly, this invention provides in one of its embodiments a method of providing microbiological control in an aqueous medium such as recreational water, industrial cooling water, process water, or wastewater, and preferably in water having a pH of at least about 8.0 such as cooling water and/or eradication or reduction of biofilm on a surface in

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contact with such aqueous medium, which method comprises introducing into the aqueous medium a microbiocidally effective amount of at least one 1,3-dibromo-5,5-dialkylhydantoin in which one of the alkyl groups in the 5-position is a methyl group and the other alkyl group in the 5-position contains in the range of 1 to 4 carbon atoms (DBDAH), (i) the molar quantity of the DBDAH introduced being less than the molar quantity of N,N'-bromochloro-5, 5-dimethylhydantoin (BCDMH) that would be required to effect the same degree of microbiological control in such medium, (ii) the quantity of DBDAH introduced into such aqueous medium releasing an amount of "free chlorine" that is greater than the amount of "free chlorine" that would be released in such medium by an equimolar quantity of BCDMH, and (iii) the amount of "free chlorine" released by the quantity of such at least one DBDAH introduced into such aqueous medium being greater than the amount of "free chlorine" that could be predicted to be released by that quantity of DBDAH on the basis of the amount of "free chlorine" that would be released in such medium by an equimolar quantity of BCDMH. The most preferred DBDAH used in this embodiment is 1,3-dibromo-5,5-dimethylhydantoin (DBDMH).

In another of its embodiments this invention provides a method of effecting microbiocidal activity in water preferably but not necessarily having a pH of at least about 8.0, which method comprises providing in such water using a 1,3-dibromo-5,5-dialkylhydantoin (DBDAH) microbiocidal agent in which one of the alkyl groups of the DBDAH in the 5-position is a methyl group and the other alkyl group in the 5-position contains in the range of 1 to 4 carbon atoms, a microbiocidally effective amount of "free chlorine" that is greater than could be predicted from the amount of "free chlorine" that would be released by an equimolar quantity of N,N'-bromochloro-5,5-dimethylhydantoin (BCDMH) in such water, while using a smaller molar quantity of the DBDAH than the molar quantity of BCDMH required to release such microbiocidally effective amount of "free chlorine". 1,3-dibromo-5,5-dimethylhydantoin (DBDMH) is also the most preferred microbiocidal agent employed in this embodiment.

A further embodiment of this invention is a composition having microbiocidal activity, which composition comprises water preferably but not necessarily having a pH of at least about 8.0 to which has been added a microbiocidally effective quantity of a 1,3-dibromo-5,5-dialkylhydantoin (DBDAH) in which one of the alkyl groups is a methyl group and the other alkyl group contains in the range of 1 to 4 carbon atoms, (i) the molar quantity of the DBDAH added being less than the molar quantity of N,N'-bromochloro-5, 5-dimethylhydantoin (BCDMH) that would be required to effect the same degree of microbiocidal activity in that water, (ii) the quantity of DBDAH added releasing an amount of "free chlorine" that is greater than the amount of "free chlorine" that would be released in that water by an equimolar quantity of BCDMH, and (iii) the amount of "free chlorine" released by the amount of DBDAH added being greater than the amount of "free chlorine" that could be predicted to be released by DBDAH on the basis of the amount of "free chlorine" that would be released in that water by an equimolar quantity of BCDMH. Here again, the most preferred DBDAH is 1,3-dibromo-5,5-dimethylhydantoin (DBDMH).

This invention as reflected for example by the above embodiments, involves a number of surprising features. First of all, it is surprising that to achieve a given level of microbiocidal effectiveness, especially in an aqueous

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medium with a pH of at least about 8.0, a smaller quantity of DBDAH such as DBDMH can be used than BCDMH. Heretofore the art has regarded BCDMH as being a biocidal agent of choice because of the levels of effectiveness achieved by use of that agent. Moreover, it is surprising that in an aqueous medium preferably but not necessarily with a pH of about 8.0 or higher, the amount of "free chlorine" released by a DBDAH such as DBDMH is greater than the amount of "free chlorine" released by an equimolar quantity of BCDMH. At best the expectation would be that there could be no significant difference, and thus that there would be no appreciable difference, in these respective amounts of "free chlorine". Furthermore, not until comparative testing of water samples with a pH of greater than about 8.0 containing, respectively, equimolar quantities of DBDMH or BCDMH for "free chlorine" using Hach Method 8021 (copyright 1997, by Hach Company) and for "total chlorine" using Hach Method 8167 (copyright 1997, by Hach Company), and converting the mg/L Cl₂ "free chlorine" values from the tests to percentages of the mg/L Cl₂ "total chlorine" values from the tests, was the unpredictable superiority of DBDMH in releasing larger amounts of "free chlorine" than the equimolar quantity of BCDMH discovered. Prior to such testing there was no way of predicting the existence this superiority.

As a consequence of the above surprising features of this invention it is now possible to achieve the same microbiocidal effect on or control of bacteria, algae, biofilm, and like microbiological entities as given by BCDMH but using smaller molar amounts of one or more of the above described 1,3-dibromo-5,5-dialkylhydantoins such as DBDMH, and at the same time significantly reducing the amounts of halogenated materials to be released to the environment. Alternatively, greater microbiocidal control of bacteria, algae, biofilm, and like microbiological entities can be achieved using one or more of the above described 1,3-dibromo-5,5-dialkylhydantoins such as DBDMH in the same molar quantity as BCDMH, or even somewhat less molar quantity of one or more such 1,3-dibromo-5,5-dialkylhydantoins than BCDMH.

Another embodiment of this invention is a method for determining a quantity of a 1,3-dibromo-5,5-dialkylhydantoin such as DBDMH to be used in microbiocidal treatment of water preferably but not necessarily having a pH of at least about 8.0. The method comprises (i) determining the "free chlorine" concentrations of samples of said water containing respectively DBDMH and the DBDAH, (ii) determining the "total chlorine" values of samples of said water containing respectively BCDMH and DBDAH, and (iii) determining respectively for BCDMH and DBDAH the relative extent of hydrolysis to species which register as "free chlorine". Such determinations can be accomplished by dividing the value obtained for "free chlorine" by the value obtained for "total chlorine" and multiplying the quotient by 100 to obtain the percentage of hydrolysis to "free chlorine". Use of this method enables the amount of DBDAH to be used in achieving the target dose of "free chlorine". By "target dose" is meant the dose deemed suitable by the water treater to effect microbiocidal control in the water being subjected to treatment. In conducting this embodiment of the invention, any suitable method of determining "free chlorine" and "total chlorine" can be used, but in the event of any conflicting data as between different parties, Hach Method 8021 (copyright 1997) for "free chlorine" and Hach Method 8167 (copyright 1997) for "total chlorine" shall be used. For example, a given water treater may deem a slug dose of, say, 0.2 mg/L

of "free chlorine" to be sufficient for maintaining microbiocidal control in a given body of water. Knowing the extent of hydrolysis as determined by use of this invention, and also the total volume of the body of water, the water treater can determine an amount of solid DBDAH to apply in a slug dose to achieve effective microbiocidal control while at the same time without using an undue excess of DBDAH.

In another of its embodiments, this invention provides a method of effecting biocidal activity in water preferably but not necessarily having a pH of at least about 8.0, which method comprises providing in such water using a 1,3-dibromo-5,5-dialkylhydantoin (DBDAH) biocidal agent an amount of "free chlorine" that is greater than could be predicted from the amount of "free chlorine" provided by an equimolar amount of N,N'-bromochloro-5,5-dimethylhydantoin (BCDMH), as determinable by comparative testing as follows:

   a) determining the amount of species of the DBDAH and of BCDMH which register respectively as "total chlorine" using Hach Method 8167 (copyright 1997, by Hach Company);

   b) determining the amount of species of the DBDAH and of BCDMH which register respectively as "free chlorine" using Hach Method 8021 (copyright 1997, by Hach Company); and

   c) determining respectively for the DBDAH and BCDMH the relative extent of hydrolysis to species which register as "free chlorine".

The foregoing method can be applied for treating water for microbiological control and/or for biofilm eradication.

Another embodiment is water preferably but not necessarily having a pH of at least about 8.0 in which microbiological and/or biofilm activity is minimized if not eliminated by the addition thereto of an amount of "free chlorine" using an above-described 1,3-dibromo-5,5-dialkylhydantoin (DBDAH) biocidal agent where the amount of "free chlorine" actually present in the water is greater than could be predicted from the amount of "free chlorine" provided by an equimolar amount of N,N'-bromochloro-5,5-dimethylhydantoin (BCDMH), as determinable by comparative testing as follows:

   a) determining the amount of species of the DBDAH and of BCDMH which register respectively as "total chlorine" using Hach Method 8167 (copyright 1997, by Hach Company); and

   b) determining the amount of species of the DBDAH and of BCDMH which register respectively as "free chlorine" using Hach Method 8021 (copyright 1997, by Hach Company); and

   c) determining respectively for the DBDAH and BCDMH the relative extent of hydrolysis to species which register as "free chlorine".

The microbiological control and/or for biofilm eradication in the water involves effective biocidal activity against such organisms and pathogens as bacteria, algae, and biofilms.

Other embodiments, features, and advantages of this invention will be still further apparent from the ensuing description and appended claims.

BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 is a graphical representation of the results of standard "free chlorine" and "total chlorine" tests performed on simulated cooling water solutions dosed with BCDMH or DBDMH, all as described in detail in Example 1 hereinafter.

FIG. 2 is a graphical representation of the percent of hydrolysis experienced by the respective test samples of BCDMH and of DBDMH in the tests performed in Example 1.

FURTHER DETAILED DESCRIPTION

At the outset it should be understood that the terms "free chlorine" and "total chlorine" are terms commonly used by persons in the fields of industrial and recreational water treatment. The values for the levels of "free chlorine" and "total chlorine" in the water are determined by use of appropriate standard test procedures which differentiate between the two. Further, the terms "free chlorine" and "total chlorine" are not restricted to just chlorine species in the water but rather, include certain bromine species in the water as well. Thus in a case where a biocidal agent used in treating the water contains both bromine and chlorine atoms (e.g., BCDMH), the "free chlorine" and "total chlorine" levels determined in the respective appropriate test procedures used would include quantification of the sum of the bromine species and chlorine species present that respond to the respective tests. The sum of these respective levels is reported, however, as "free chlorine" or "total chlorine", depending on the test used. Similarly, if the water treating agent used contains bromine atoms but no chlorine atoms, the "free chlorine" and "total chlorine" levels determined in the respective appropriate standard test procedures used would involve quantification of the level of bromine species present that respond to the respective tests. Thus although the halogen species actually present in such case are bromine-containing species, the levels present as determined in the respective tests would be reported as "free chlorine" and "total chlorine", respectively.

Heretofore it has been universally believed that all bromine species dissolved in the water respond positively in the standard "free chlorine" test procedure. However, one of the features of this invention is the discovery that this universal belief is erroneous when the "free chlorine" test procedure is applied to recreational water, cooling water, process water, and wastewater, that contains bromine species, and especially to cooling water, process water, and wastewater that is has a pH above about 8.0. Under these conditions the dibromo-containing microbiocides used pursuant to this invention can give vastly superior values for "free chlorine" as compared to the corresponding bromochloro microbiocides as evidenced by the results described herein in which comparisons were made between DBDMH and BCDMH.

For example, it has been found that when water having a pH above about 8.0 is treated with BCDMH to reach a desired "free chlorine" level, the amount of BCDMH being used is far greater than necessary to achieve a given level of microbiocidal effectiveness. This in turn means that the consumer has purchased and is using much more of the microbiocidal agent than necessary. As a consequence, there are involved both an economic penalty due to excessive consumption, and an environmental penalty due to release of excessive quantities of less biocidally-active halogen species to the environment.

Nevertheless, the "free chlorine" level in water treated with a halogen-releasing biocidal agent remains the yardstick by which microbiocidal performance is measured. Species which respond to the standard "free chlorine" test are HOCl and HOBr. Any other form of soluble halogen species do not respond to the standard "free chlorine" test. Such non-responsive species include, for example, chlorine species bound to a nitrogen atom. On the other hand, the standard "total chlorine" test measures both HOBr and HOCl, and any halogen species that do not respond to the standard "free chlorine " test.

The standard tests for determination of "free chlorine" and "total chlorine" are based on classical test procedures

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devised by Palin in 1974. See A. T. Palin, "Analytical Control of Water Disinfection With Special Reference to Differential DPD Methods For Chlorine, Chlorine Dioxide, Bromine, Iodine and Ozone", *J. Inst. Water Eng.,* 1974, 28, 139. While there are various modernized versions of the Palin procedures, the version of the tests for "free chlorine" and "total chlorine" used and to be used as the standard in connection with this invention, are fully described in Hach *Water analysis Handbook,* 3rd edition, copyright 1997. The procedure for "free chlorine" is identified in that publication as Method 8021 appearing on page 335, whereas the procedure for "total chlorine" is Method 8167 appearing at page 379. Briefly, the "free chlorine" test involves introducing to the halogenated water a powder comprising DPD indicator powder and a buffer. "Free chlorine" present in the water reacts with the DPD indicator to produce a red to pink coloration. The intensity of the coloration depends upon the concentration of "free chlorine" species present in the sample. This intensity is measured by a calorimeter calibrated to transform the intensity reading into a "free chlorine" value in terms of mg/L Cl_2. Similarly, the "total chlorine" test also involves use of DPD indicator and buffer. In this case, KI is present with the DPD and buffer whereby the halogen species present, including nitrogen-combined halogen, reacts with KI to yield iodine species which turn the DPD indicator to red/pink. The intensity of this coloration depends upon the sum of the "free chlorine" species and all other halogen species present in the sample. Consequently, this coloration is transformed by the colorimeter into a "total chlorine" value expressed as mg/L Cl_2.

A halogen water treating agent which could provide a high level of both "free chlorine" and "total chlorine" and where these levels would be close together would be a very desirable water treating agent. Such an agent would be highly effective as a microbiocidal agent and if of an appropriate chemical structure, could be environmentally friendly and highly cost-effective. Pursuant to this invention these criteria are met by certain water-soluble 1,3-dibromo-5,5-dialkylhydantoins (DBDAH).

In particular, the water-soluble 1,3-dibromo-5,5-dialkylhydantoins utilized in the practice of this invention are those in which one of the alkyl groups in the 5-position is a methyl group and the other alkyl group in the 5-position is an alkyl group having in the range of 1 to 4 carbon atoms. Thus the biocides used in this invention comprise 1,3-dibromo-5,5-dimethylhydantoin, 1,3-dibromo-5-ethyl-5-methylhydantoin, 1,3-dibromo-5-n-propyl-5-methylhydantoin, 1,3-dibromo-5-isopropyl-5-methylhydantoin, 1,3-dibromo-5-n-butyl-5-methylhydantoin, 1,3-dibromo-5-isobutyl-5-methylhydantoin, 1,3-dibromo-5-sec-butyl-5-methylhydantoin, 1,3-dibromo-5-tert-butyl-5-methylhydantoin, and mixtures of any two or more of them. Of these biocidal agents, 1,3-dibromo-5-isobutyl-5-methylhydantoin, 1,3-dibromo-5-n-propyl-5-methylhydantoin and 1,3-dibromo-5-ethyl-5-methylhydantoin are, respectively, preferred, more preferred, and even more preferred members of this group from the cost effectiveness standpoint. Of the mixtures of the foregoing biocides that can be used pursuant to this invention, it is preferred to use 1,3-dibromo-5,5-dimethylhydantoin as one of the components, with a mixture of 1,3-dibromo-5,5-dimethylhydantoin and 1,3-dibromo-5-ethyl-5-methylhydantoin being particularly preferred. The most preferred biocide employed in the practice of this invention is 1,3-dibromo-5,5-dimethylhydantoin.

When a mixture of two or more of the foregoing biocides is made up or used pursuant to this invention, the individual biocides of the mixture can be in any proportions relative to each other.

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It is to be understood that in the practice of this invention it is not necessary to perform the specified tests every time a body of water is to be dosed with DBDAH or with BCDMH (depending upon the embodiment of this invention being practiced). Instead, as made clear by the use of the term "determinable" (i.e., able to be determined), the testing should be done when deemed necessary or desirable to either establish the requisite dosage of DBDAH or BCDMH, as the case may be, or to check or confirm that the proposed dosage complies with this invention and thus will make available the economic and environmental benefits resulting from the practice of this invention.

When it is desired to conduct the appropriate testing any suitable method of determining "free chlorine" and "total chlorine" can be used, but in the event of any conflicting data or dispute as between different parties, the full procedure set forth below entitled "DBDAH and BCDMH Test Procedure" is to be used to resolve the issue in connection with any embodiment of this invention.

DBDAH and BCDMH Test Procedure

1. To determine the amount of species present in the water which respond to the "free chlorine" and "total chlorine" tests, the water sample should be analyzed within a few minutes of being taken, and preferably immediately upon being taken.

2. Hach Method 8021 for testing the amount of species present in the water sample which respond to the "free chlorine" test involves use of the Hach Model DR 2010 calorimeter. The stored program number for chlorine determinations is recalled by keying in "80" on the keyboard, followed by setting the absorbance wavelength to 530 nm by rotating the dial on the side of the instrument. Two identical sample cells are filled to the 10 mL mark with the water under investigation. One of the cells is arbitrarily chosen to be the blank. Using the 10 mL cell riser, this is admitted to the sample compartment of the Hach Model DR 2010, and the shield is closed to prevent stray light effects. Then the ZERO key is depressed. After a few seconds, the display registers 0.00 mg/L Cl_2. To second cell, the contents of a DPD Free Chlorine Powder Pillow are added. This is shaken for 10–20 seconds to mix, as the development of a pink-red color indicates the presence of species in the water which respond positively to the DPD test reagent. Within one minute of adding the DPD "free chlorine" reagent to the 10 mL of water in the sample cell, the blank cell used to zero the instrument is removed from the cell compartment of the Hach Model DR 2010 and replaced with the test sample to which the DPD "free chlorine" test reagent was added. The light shield is then closed as was done for the blank, and the READ key is depressed. The result, in mg/L Cl_2 is shown on the display within a few seconds. This is the "free chlorine" level of the water sample under investigation. Hach Method 8167 for testing the amount of species present in the water sample which respond to the "total chlorine" test involves use of the Hach Model DR 2010 calorimeter. The stored program number for chlorine determinations is recalled by keying in "80" on the keyboard, followed by setting the absorbance wavelength to 530 nm by rotating the dial on the side of the instrument. Two identical sample cells are filled to the 10 mL mark with the water under investigation. One of the cells is arbitrarily chosen to be the blank. To the second cell, the contents of a DPD Total Chlorine Powder Pillow are added. This is shaken for 10–20 seconds to mix, as the development of a pink-red color

indicates the presence of species in the water which respond positively to the DPD "total chlorine" test reagent. On the keypad, the SHIFT TIMER keys are depressed to commence a three minute reaction time. After three minutes the instrument beeps to signal the reaction is complete. Using the 10 mL cell riser, the blank sample cell is admitted to the sample compartment of the Hach Model DR 2010, and the shield is closed to prevent stray light effects. Then the ZERO key is depressed. After a few seconds, the display registers 0.00 mg/L Cl_2. Then, the blank sample cell used to zero the instrument is removed from the cell compartment of the Hach Model DR 2010 and replaced with the test sample to which the DPD "total chlorine" test reagent was added. The light shield is then closed as was done for the blank, and the READ key is depressed. The result, in mg/L Cl_2 is shown on the display within a few seconds. This is the "total chlorine" level of the water sample under investigation.

The various new features of this invention and the advantages accruing therefrom will be further apparent from Examples 1–3, which as presented for purposes of illustrating the invention without limiting the scope thereof.

EXAMPLE 1

Simulated cooling water was prepared using deionized water to which calcium chloride and sodium bicarbonate were added to provide calcium hardness of 400 ppm and a total alkalinity of 300 ppm. A small amount of phosphonobutanetricarboxylic acid (PBTC) (5 ppm) was used to prevent calcium carbonate precipitation. Concentrated sodium hydroxide solution was added to adjust the pH of the simulated cooling water solutions to pH 9.1.

Stock solutions of DBDMH and of BCDMH were prepared by slurrying 1 gram of the respective powders in 100 mL of deionized water. After stirring for 20 minutes, the insolubles were filtered to yield clear saturated stock solutions of DBDMH and BCDMH, respectively. Iodometric titration of the stock solutions using the potassium iodide-sodium thiosulfate method indicated the DBDMH solution contained 580 mg/L (as total chlorine), and the BCDMH solution contained 1100 mg/L (as total chlorine).

The stock solutions were used to dose two simulated cooling water solutions to 1 mg/L as total chlorine. Thus, 1.7 mL of DBDMH stock solution was introduced to 1000 mL of simulated cooling water to form a first test solution, and 0.91 mL of BCDMH stock solution was introduced to another 1000 mL of simulated cooling water to produce a second test solution. Both of these test solutions were placed in screw-capped amber bottles to shield form light and prevent evaporation. The bottles were then placed in an oven and heated to 38° C. (100° F.). As soon as the solutions reached the equilibrium temperature of 38° C., 10 mL aliquots of each test solution were removed and analyzed using Hach Method 8167 for "total chlorine", to confirm that each contained a "total chlorine" level of 1 mg/L. The same solutions were also analyzed using Hach Method 8021 for "free chlorine" to determine how much of the total chlorine species also registered as "free chlorine". These analyses were recorded as results at time 0. The test solutions were then kept in the oven at the equilibrium temperature of 38° C. for a total of 6 hours during which time additional 10 mL aliquots were removed at known time intervals and subjected to the same analysis procedures for "free chlorine" and "total chlorine".

The results of each of the foregoing determinations are summarized in Table 1 and are depicted graphically in FIG. 1. In Table 1 the values given at times 0.5 through 6 hours are percentages of the corresponding values shown in Table 1 for Time 0. These results are depicted graphically in FIG. 1. Table 2 sets forth the percentages of hydrolysis to "free chlorine" experienced by the BCDMH and the DBDMH based on the results shown in Table 1. FIG. 2 depicts the results given in Table 2. It can be seen from Table 2 and FIG. 2 that over a time span of 6 hours the differences in the percentage of hydrolysis as between BCDMH and DBDMH remained substantially constant. The minor variations in such differences appearing in Table 2 and FIG. 2 are deemed insignificant statistically inasmuch as they are within experimental error.

TABLE 1

Time, hr	BCDMH Free Cl_2	BCDMH Total Cl_2	DBDMH Free Cl_2	DBDMH Total Cl_2
0	23.1	100	98.8	100
0.5	25.6	104	100	104
1	23.1	100	85.1	87.3
1.5	17.9	92.3	87.3	87.3
2	16.6	88.5	81.6	83.9
3	16.6	88.5	70.1	74.7
4	30.7	79.5	65.5	66.6
5	15.4	76.9	60.1	63.2
6	10.2	71	59.8	62

TABLE 2

Time, hr	BCDMH % hydrolysis to Free Cl_2	DBDMH % hydrolysis to Free Cl_2
0	23.1	98.8
0.5	24.7	95.6
1	23.1	97.3
1.5	19.4	100
2	18.8	97.2
3	18.8	93.8
4	38.7	93.8
5	20	96.4
6	14.3	96.3

EXAMPLE 2

The effectiveness of DBDMH and of BCDMH in microbiological control in cooling tower water was investigated in comparative tests. The cooling tower consisted of two 500-ton units in a crossflow design. The total system-contained volume was 14,000 gallons, and the tower contained medium efficiency film fill. Water from the tower cooled the coils of two 300-ton air conditioners (chillers). The tower typically operated at a pH of about 9.1 and 4 cycles of concentration. Blowdown was controlled by conductivity. Make-up water consisted of softened city water and which was of good quality. The make-up water was very low in calcium (<10 mg/L) but high in pH (8.7). The alkalinity was 145 mg/L (as $CaCO_3$), and the silica level was 28 mg/L. The tower employed a conventional polyphosphate/molybdate/phosphonate program to provide corrosion and deposit control. The conditions and results are summarized in Table 3.

TABLE 3*

Cooling Tower Data	Cooling Tower Water	Make-up Water
Temperature (return line)	91° F.	—
Temperature (to process)	83° F.	—
Δ T	8° F.	—
Make-up water	4800 gal/day	—
Water Chemistry		
Conductivity, mS/cm	1.22	0.32
pH, units	9.2	8.7
Alkalinity, mg/L as CaCO₃	480	145
Total Hardness, mg/L as CaCO₃	1	3
Silica, mg/L	100	28

*This data represents the average of several analyses conducted during the course of the field trial.

The BCDMH (20 lbs) was introduced to the water using 20-gram, 1-inch tablets charged to a solid halogen feeder (Neptune model BT-40, Neptune Chemical Pump Co., Inc., Lansdale, Pa.). Before each dose, the cooling tower water was sampled and enumerated for heterotrophic bacteria plate counts. The tower was slug dosed three times a week with BCDMH. Slug dosing was accomplished by diverting through the feeder containing the tablets a sidestream of the recirculating water for about 1 to 5 hours until a "free chlorine" dose of about 0.5 mg/L (as "free chlorine") was obtained. The "total chlorine" dose was measured at the same time. After each dose the cooling water was sampled and enumerated for heterotrophic bacteria plate counts. As necessary, the feeder was replenished with more BCDMH tablets. The total dry weight of BCDMH tablets consumed over a 30-day test period (obtained by subtracting the dry weight of the tablets remaining in the feeder at the completion of the test from the total dry weight of the tablets added to the feeder during the test period) was found to be 25 lbs.

It was found that this biocide program (biocide dose 0.5 mg/L "free chlorine") reduced heterotrophic bacterial levels in the bulk water by an average of 1 order of magnitude. For example, before the biocide dose the bacteria levels in the bulk water ranged from 10⁵ to 10⁴ CFUs/mL. After the biocide dose the bacteria levels in the bulk water were reduced to 10⁴ to 10³.

After emptying the feeder of BCDMH tablets, 20 lbs of DBDMH granules were charged into the feeder. Thereupon the same procedure as described above for the BCDMH was carried out except for the fact that it was unnecessary to add any additional DBDMH to the feeder during the 30-day test period. In fact, the total weight of DBDMH consumed during the test was only 7 lbs. Also, the targeted 0.5 mg/L "free chlorine" dose in the bulk water was achieved in only 20 to 30 minutes. It was found that the biocidal performance provided by 7 lbs of DBDMH was the same as provided by 25 lbs of BCDMH under the same test conditions.

EXAMPLE 3

Using the same cooling tower as used in Example 2, the effectiveness of 1,3-dibromo-5,5-dimethylhydantoin in microbiological control in cooling tower water was investigated. As noted above, the cooling tower consisted of two 500-ton units in a crossflow design. The total system-contained volume was 14,000 gallons, and the tower contained medium efficiency film fill. Water from the tower cooled the coils of two 300-ton air conditioners (chillers). The tower typically operated at a pH about 9.1 and 4 cycles of concentration. Blowdown was controlled by con-

ductivity. Make-up water consisted of softened city water and which was of good quality. The make-up water was very low in calcium (<10 mg/L) but high in pH (8.7). The alkalinity was 145 mg/L (as CaCO₃), and the silica level was 28 mg/L. The tower employed a conventional polyphosphate/molybdate/phosphonate program to provide corrosion and deposit control.

The 1,3-dibromo-5,5-dimethylhydantoin was introduced to the water using granules charged to a solid halogen feeder (Neptune model BT-40, Neptune Chemical Pump Co., Inc., Lansdale, Pa.). The field trial lasted 51 days. The tower was slug dosed three times a week with 1,3-dibromo-5,5-dimethylhydantoin. Slug dosing was accomplished by diverting a sidestream of the recirculating water through the feeder containing the granules for about 1 to 5 hours until a total halogen residual of about 0.75 mg/L (as Cl₂) was obtained. This biocide program reduced bacterial levels in the bulk water by an average of 2 orders of magnitude, with bacteria levels in the bulk water after the biocide dose ranging from 10¹ to 10³ CFUs/mL.

The results from the average of several analyses conducted during the course of this field trial using DBDMH were as follows: In the microbiological tests, the levels of aerobic bacteria were in the range of 6×10⁰ to 3×10⁵ CFUs/mL in the cooling tower water and 10⁰ in the make-up water. As regards water chemistry, the free halogen residual (as Cl₂) was 0.79 mg/L (the range being 1.9–0.00 mg/L) in the cooling tower water and 0.05 mg/L in the make-up water; and the total halogen residual (as Cl₂) was 0.82 mg/L (the range being 1.9–0.03 mg/L) in the cooling tower water and 0.8 mg/L in the make-up water.

The DBDMH utilized in the practice of this invention can be in the form of a powder, granules, caplets, tablets, briquettes, or pucks. A preferred process for producing highly suitable powder or particulate DBDMH and novel DBDMH products are described respectively in commonly-owned copending application Ser. Nos. 09/484,844 and 09/484,687, both filed Jan. 18, 2000. Methods for the formation of compacted forms of DBDMH such as caplets, tablets, briquettes and pucks are described in commonly-owned copending application Ser. No. 09/487,816, filed Jan. 18, 2000. Methods for producing DBDMH in granular form are described in commonly-owned copending application Ser. No. 09/483,896, filed Jan. 18, 2000. The disclosures of each of the foregoing applications are incorporated herein by reference as if fully set forth herein.

The methods of this invention thus involve use of 1,3-dibromo-5,5-dimethylhydantoin in compacted or in non-compacted forms. When used in compacted forms, the compacted forms can be produced without use of a binder provided that the average particle size of the 1,3-dibromo-5,5-dimethylhydantoin is at least 175 microns. Alternatively and more preferably, the compacted forms can be produced with use of a binder. A preferred type of binder for producing such compacted products is a saturated, normally solid, fatty amide as described in U.S. Pat. No. 5,565,576, issued Oct. 15, 1996 to L. K. Hall, J. A. Falter, and T. E. Farina, the disclosure of which patent is incorporated herein in toto as if fully set forth herein. In the practice of this invention such fatty amide binder is used with 1,3-dibromo-5,5-dimethylhydantoin having an average particle size of at least 175 microns. A particularly preferred type of binder for use in producing the compacted forms of 1,3-dibromo-5,5-dimethylhydantoin for use in this invention is a micronized synthetic polyolefin-based hydrocarbon wax and/or a micronized synthetic polyfluorocarbon wax effective to form the compacted product, provided the wax is suitably

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compatible with the 1,3-dibromo-5,5-dimethyhydantoin. In the practice of this invention with compacted forms of blends of 1,3-dibromo-5,5-dimethylhydantoin with a micronized synthetic polyolefin-based hydrocarbon wax and/or a micronized synthetic polyfluorocarbon wax, the average particle size of the 1,3-dibromo-5,5-dimethylhydantoin can be in the range of about 20 to about 600 microns, but preferably the average particle size of the 1,3-dibromo-5,5-dimethylhydantoin is in the range of about 175 to about 400 microns, if not even greater.

The amount of 1,3-dibromo-5,5-dimethylhydantoin used in practicing the methods of this invention is a biocidally effective amount, e.g., an amount which is at least sufficient to achieve substantial microbiological control, if not complete microbiological control, in the water being treated and/or substantial biofilm eradication, if not complete biofilm eradication, from the surfaces in contact with the water system being treated. Typically, dosages of 1,3-dibromo-5,5-dimethylhydantoin used for this purpose will fall within the range of about 0.1 to about 4.5 milligrams of "free chlorine" per liter of water (which corresponds to about 0.2 to about 10 milligrams of bromine, as Br₂, per liter of water). Preferably, such dosages are in the range of about 0.1 to about 2 milligrams of "free chlorine" per liter of water (which corresponds to about 0.2 to about 5 milligrams of bromine, as Br₂, per liter of water). However, departures from these ranges are permissible and are within the scope of this invention, provided that the departures result in sufficient microbiological control in accordance with the needs of the occasion, including applicable governmental regulations.

As noted above, the most effective presently-known process for producing 1,3-dibromo-5,5-dimethylhydantoin for use in the practice of this invention is described in commonly-owned copending application Ser. No. 09/484, 844, filed Jan. 18, 2000. That process comprises, for example, concurrently feeding (i) an aqueous solution or slurry formed from an inorganic base and 5,5-dimethylhydantoin, and (ii) abrominating agent in proportions such that each nitrogen atom is substituted by a bromine atom, thereby continuously forming product which precipitates in an aqueous reaction mixture. The pH of the mixture is continuously maintained in the range of about 5.5 to about 8.5. Examples 4–14 below illustrate that process. In Examples 4–14, pH was monitored by use of a pH meter. In Examples 4–13, bromine was fed using a Cole-Parmer Masterflex computerized drive and Easy-Load® pump head. When conducting the continuous operations of Examples 12 and 13, the resulting reaction slurry was collected manually and intermittently from the bottom of the reactor. Each fraction was collected in a 500 ml flask. These Examples do not constitute part of this invention. Instead they are presented to show best ways of making DBDMH.

EXAMPLE 4

235 Grams of NaOH (5.85 mol) are dissolved in 1800 g of water, and 375 g of 5,5-dimethylhydantoin (2.93 mol) are added to the NaOH solution. There are 935 g of Br₂ (5.85 mol) in the bromine reservoir. A 1-liter jacketed flask into which the Br₂ and the 5,5-dimethylhydantoin/NaOH solution are fed is maintained at 25° C. with a cooling bath. The 5,5-dimethylhydantoin/NaOH solution is co-fed to the reaction flask simultaneously with, but separately from, Br₂. The feed of the 5,5-dimethylhydantoin/NaOH solution was initiated shortly before (e.g., 3–4 min.) the initiation of the Br₂ feed. The feed rate of the 5,5-dimethylhydantoin/NaOH solution is 10 mL/minute, and the feed rate of the Br₂ is

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1.60–1.70 mL/minute. The reaction mixture is stirred with a mechanical stirrer at a rate of 350–400 rpm. During the reaction, the pH ranged from 7.4 to 7.9. The slurry that forms as the reaction progresses is collected at a rate such that the level of the solution in the reaction flask remains constant. 500 mL fractions of product are collected through the bottom of the reaction flask, in an average time of 30 minutes per fraction. When the 5,5-dimethylhydantoin/NaOH solution feed is finished, 86 g of Br₂ (0.54 mol) remains in the bromine reservoir.

Each product fraction is filtered and washed with three 500 mL portions of water, and the solid is then dried under a stream of nitrogen. The isolated yield of 1,3-dibromo-5, 5-dimethylhydantoin is 673 g, a yield of 80% based on 5,5-dimethylhydantoin, or a yield of 89% based on Br₂. The active bromine content is at least 99%, as determined by iodometric titration.

EXAMPLE 5

44 Grams of NaOH (1.1 mol) are dissolved in 338 g of water, and 70.4 g of 5,5-dimethylhydantoin (0.55 mol) is added to the NaOH solution. There are 175.1 g of Br₂ (1.1 mol) in the bromine reservoir. The reaction flask into which the Br₂ and the 5,5-dimethylhydantoin/NaOH solution are fed is maintained at 35° C. with a heating bath. The reaction flask is charged with ~200 mL heel (238 g) of a 1,3-dibromo-5,5-dimethylhydantoin filtrate (mother liquor). The 5,5-dimethylhydantoin/NaOH solution is co-fed to the reaction flask simultaneously with, but separately from, Br₂. The reaction mixture is stirred with a mechanical stirrer at a rate of 400 rpm. During the reaction, the pH ranged from 6.9 to 8.0. The reaction temperature stabilized at 37° C. during the 0.5 hour addition time. When the addition of reagents is finished, the orange slurry is filtered at 35° C. and washed with 650 mL of water. The resultant white solid is dried overnight under a stream of nitrogen. The isolated yield of 1,3-dibromo-5,5-dimethylhydantoin is 147.6 g, a yield of 94%, and the active bromine content of the 1,3-dibromo-5, 5-dimethylhydantoin is 55.1 wt % (98.66% of the theoretical value), as determined by iodometric titration. cl EXAMPLE 6

44 Grams of NaOH (1.1 mol) are dissolved in 338 g of water, and 70.4 g of 5,5-dimethylhydantoin (0.55 mol) is added to the NaOH solution. There are 172.0 g of Br₂ (1.07 mol) in the bromine reservoir. The reaction flask into which the Br₂ and the 5,5-dimethylhydantoin/NaOH solution are fed is maintained at 67° C. with a heating bath. The reaction flask is charged with ~200 mL heel (238 g) of a 1,3-dibromo-5,5-dimethylhydantoin filtrate (mother liquor). The 5,5-dimethylhydantoin/NaOH solution is co-fed to the reaction flask simultaneously with, but separately from, Br₂. The bromine is diluted with nitrogen and fed below the surface of the solution in the reaction flask. The reaction mixture is stirred with a mechanical stirrer at a rate of 400 rpm; the pH ranged from 6.7 to 7.1 during the reaction. During the 0.5 hour addition time, the reaction temperature stabilized at 67° C. When the addition of reagents is finished, the orange slurry is discharged from the reaction flask into a beaker and allowed to cool slowly. The slurry is filtered at ~45° C. and washed with two 500 mL portions of water. The resultant white solid is dried overnight under a stream of nitrogen. The isolated yield of 1,3-dibromo-5,5-dimethylhydantoin is 130.5 g, a yield of ~83% based on 5,5-dimethylhydantoin, or a yield of ~85% based on Br₂. The active bromine content of the 1,3-dibromo-5,5-dimethylhydantoin is 55.9 wt % (100% of the theoretical value), as determined by iodometric titration. Particle size data on the 1,3-dibromo-5,5-

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dimethylhydantoin product formed in this operation based on a representative dried sample of the product are summarized in Table 4.

TABLE 4

Particle Size Category	Particle Size of Product
Average	237.5μ
10% is greater than	371.6μ
25% is greater than	309.8μ
50% is greater than	239.1μ
75% is greater than	165.6μ
90% is greater than	99.81μ
Range	0.040–541.9μ

EXAMPLE 7

354 Grams of NaOH (8.85 mol) are dissolved in 2700 g of water. 562 g of 5,5-dimethylhydantoin (4.386 mol) is added to the NaOH solution. The reaction flask is charged with 500 mL heel of a 1,3-dibromo-5,5-dimethylhydantoin filtrate (mother liquor). The 5,5-dimethylhydantoin/NaOH solution is co-fed to the jacketed reaction flask, no heating or cooling is applied simultaneously with, but separately from, Br$_2$. The feed rate of the 5,5-dimethylhydantoin/NaOH solution is 10 mL/minute, and the feed rate of the Br$_2$ is initially 1.70 mL/minute, but is adjusted later to 1.68 mL/minute to maintain the pH of the reaction mixture at ~7.0. The reaction mixture is stirred with a mechanical stirrer at a rate of 400 rpm reaction temperature is stabilized at about 42° C. The slurry that forms as the reaction progresses is collected at a rate such that the level of the solution in the reaction flask remains constant. Eight 500 mL fractions of product were collected through the bottom of the reaction flask, in an average time of 30 minutes per fraction. A total of 1374.5 g of Br$_2$ (8.59 mol) are added during the reaction.

Each product fraction is filtered and washed with a 500 mL portion of water; the solids are then dried overnight at 50° C. in a vacuum oven. The total isolated yield of 1,3-dibromo-5,5-dimethylhydantoin is 1152 g, a yield of 92% based on 5,5-dimethylhydantoin, or a yield of 94% based on Br$_2$. The active bromine content of the 1,3-dibromo-5,5-dimethylhydantoin ranges from 55.4 wt % to 55.7 wt % (99.1% to 99.7% of the theoretical value), as determined by iodometric titration. The average particle size of the 1,3-dibromo-5,5-dimethylhydantoin is greater than 150μ.

EXAMPLE 8

89 Grams of NaOH (2.2 mol) are dissolved in 676 g of water, and 141 g of 5,5-dimethylhydantoin (1.1 mol) is added to the NaOH solution. There are 350 g of Br$_2$ (2.2 mol) in the bromine reservoir. The reaction flask into which the Br$_2$ and the 5,5-dimethylhydantoin/NaOH solution are fed is maintained at 67° C. with a heating bath. The reaction flask is charged with ~400 mL heel (483 g) of a 1,3-dibromo-5,5-dimethylhydantoin filtrate (mother liquor). The 5,5-dimethylhydantoin/NaOH solution is co-fed to the reaction flask simultaneously with, but separately from, Br$_2$. The reaction mixture is stirred with a mechanical stirrer at a rate of 400 rpm. During the reaction, the pH ranged from 6.8 to 7.1. The reaction temperature stabilized at 67° C. during the

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66 minute addition time. When the addition of reagents is finished, the orange slurry is filtered at 43° C. and washed with 1000 mL (2×500 mL) of water. The resultant white solid is dried overnight under a stream of nitrogen. 307.3 Grams of Br$_2$ (1.92 mol) had been fed to the reaction flask. The isolated yield of 1,3-dibromo-5,5-dimethylhydantoin is 212.5 g, a yield of 77% based on Br$_2$, and 68% based on 5,5-dimethylhydantoin; the active bromine content of the 1,3-dibromo-5,5-dimethylhydantoin is 55.9 wt % (100% of the theoretical value), as determined by iodometric titration.

EXAMPLE 9

88 Grams of NaOH (2.2 mol) are dissolved in 338 g of water, and 140.8 g of 5,5-dimethylhydantoin (1.1 mol) is added to the NaOH solution. There are 352 g of Br$_2$ (2.2 mol) in the bromine reservoir. The reaction flask into which the Br$_2$ and the 5,5-dimethylhydantoin/NaOH solution are fed is maintained at 69° C. with a heating bath. The reaction flask is charged with ~200 mL heel (240 g) of a 1,3-dibromo-5,5-dimethylhydantoin filtrate (mother liquor). The 5,5-dimethylhydantoin/NaOH solution is co-fed to the reaction flask simultaneously with, but separately from, Br$_2$. The reaction mixture is stirred with a mechanical stirrer at a rate of 400 rpm. During the reaction, the pH ranged from 6.8 to 7.0. The reaction temperature stabilized at 68–69° C. during the 39 minute addition time. When the addition of reagents is finished, the orange slurry is filtered at 40° C. and washed with 500 mL of water. The resultant white solid is dried overnight under a stream of nitrogen. 285.5 Grams of Br$_2$ (1.78 mol) had been fed to the reaction flask. The isolated yield of 1,3-dibromo-5,5-dimethylhydantoin is 186.8 g, a yield of 73% based on Br$_2$, and 60% based on 5,5-dimethylhydantoin; the active bromine content of the 1,3-dibromo-5,5-dimethylhydantoin is 53.4 wt % (96% of the theoretical value), as determined by iodometric titration.

Table 5 summarizes the particle size data for the products of Examples 8 and 9.

TABLE 5

Particle Size Category	Particle Size of Product - Example 8	Particle Size of Product - Example 9
Average	210.4μ	293.6μ
10% is greater than	381.7μ	451.2μ
25% is greater than	298.3μ	349.6μ
50% is greater than	196.8μ	256.3μ
75% is greater than	115.3μ	174.9μ
90% is greater than	56.86μ	110.4μ
Range	0.040–594.9μ	0.040–>2000μ

EXAMPLE 10

44.2 Grams of NaOH (1.1 mol) are dissolved in 338 g of water, and 70.4 g of 5,5-dimethylhydantoin (0.55 mol) is added to the NaOH solution. There are 173 g of Br$_2$ (1.08 mol) in the bromine reservoir. The reaction flask into which the Br$_2$ and the 5,5-dimethylhydantoin/NaOH solution are fed is maintained at 57° C. with a heating bath. The reaction flask is charged with ~200 mL heel (244 g) of a 1,3-dibromo-5,5-dimethylhydantoin filtrate (mother liquor). The 5,5-dimethylhydantoin/NaOH solution is co-fed to the reaction flask simultaneously with, but separately from, Br$_2$. The reaction mixture is stirred with a mechanical stirrer at a rate

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of 400 rpm. During the reaction, the pH ranged from 6.8 to 7.2. Maintenance of the desired pH was accomplished by adjusting the bromine feed rate. The reaction temperature stabilized at 57° C. during the 33 minute addition time. When the addition of reagents is finished, the orange slurry is filtered at 38° C. and washed with 500 mL of water. The resultant white solid is dried overnight under a stream of nitrogen. The isolated yield of 1,3-dibromo-5,5-dimethylhydantoin is 139.8 g, a yield of 91% based on Br_2, and 89% based on 5,5-dimethylhydantoin; the active bromine content of the 1,3-dibromo-5,5-dimethylhydantoin is 55.7 wt % (99.7% of the theoretical value), as determined by iodometric titration.

EXAMPLE 11

44.2 Grams of NaOH (1.1 mol) are dissolved in 338 g of water, and 70.3 g of 5,5-dimethylhydantoin (0.55 mol) is added to the NaOH solution. There are 172.5 g of Br_2 (1.08 mol) in the bromine reservoir. The reaction flask into which the Br_2 and the 5,5-dimethylhydantoin/NaOH solution are fed is maintained at 48° C. with a heating bath. The reaction flask is charged with ~200 mL heel of a 1,3-dibromo-5,5-dimethylhydantoin filtrate (mother liquor). The 5,5-dimethylhydantoin/NaOH solution is co-fed to the reaction flask simultaneously with, but separately from, Br_2. The reaction mixture is stirred with a mechanical stirrer at a rate of 400 rpm. During the reaction, the pH ranged from 6.8 to 7.2. Maintenance of the desired pH was accomplished by adjusting the bromine feed rate. The reaction temperature stabilized at 48° C. during the 34 minute addition time. When the addition of reagents is finished, the orange slurry is filtered at 38° C. and washed with 500 mL of water. The resultant white solid is dried overnight under a stream of nitrogen. The isolated yield of 1,3-dibromo-5,5-dimethylhydantoin is 144.8 g, a yield of 94% based on Br_2, and 92% based on 5,5-dimethylhydantoin; the active bromine content of the 1,3-dibromo-5,5-dimethylhydantoin is 55.0 wt % (98.4% of the theoretical value), as determined by iodometric titration.

The particle size data for the products of Examples 10 and 11 are summarized in Table 6.

TABLE 6

Particle Size Category	Particle Size of Product - Example 10	Particle Size of Product - Example 11
Average	231.2μ	178.4μ
10% is greater than	338.3μ	281.1μ
25% is greater than	285.0μ	230.9μ
50% is greater than	228.8μ	175.7μ
75% is greater than	177.8μ	125.0μ
90% is greater than	133.0μ	79.14μ
Range	0.040–493.6μ	0.040–409.6μ

EXAMPLE 12

The process of this Example was conducted in a continuous fashion. A feed solution of 5,5-dimethylhydantoin/NaOH was formed by adding 5,5-dimethylhydantoin to a 9 wt % NaOH solution, such that the 5,5-dimethylhydantoin concentration was about 1.1 M. The 5,5-dimethylhydantoin/NaOH solution was co-fed to the reaction flask simultaneously with, but separately from, Br_2. The flask was suspended in a heating bath. The reaction mixture was stirred with a mechanical stirrer at a rate of 500 rpm. The reaction mixture was maintained at a pH of about 7.0±0.2, and the reaction temperature was maintained at 55° C. Ten fractions of product were collected in an average time of 30 minutes per fraction. The isolated yield of the 1,3-dibromo-5,5-dimethylhydantoin was 90% based on 5,5-dimethylhydantoin, and 92% based on added Br_2. The purity of the 1,3-dibromo-5,5-dimethylhydantoin, a white crystalline product, was 99.8%, based on the theoretical bromine content. Fractions 5–10 represent the particle size of the product as formed during steady-state operating conditions. Table 7 summarizes average particle size data and particle size distribution data relating to fractions 5–10 based on samples of each such fraction taken during the steady-state operation of the continuous process. The determinations showed that a bimodal distribution of the product had been produced. The overall average particle size of the product was 512.3 microns.

TABLE 7

Particle Size	Fraction 5	Fraction 6	Fraction 7	Fraction 8	Fractions 9 + 10
Average	371.7μ	445.6μ	535.5μ	560.3μ	545.9μ
10% is greater than	530.7μ	626.0μ	724.7μ	805.0μ	952.1μ
25% is greater than	462.2μ	550.9μ	643.3μ	729.3μ	833.4μ
50% is greater than	386.0μ	474.5μ	559.7μ	641.8μ	676.7μ
75% is greater than	256.8μ	369.6μ	447.8μ	436.1μ	149.6μ
90% is greater than	94.76μ	134.4μ	150.3μ	94.5μ	76.02μ
Range	0.791–786.9μ; 1255–1512μ	4.241–786.9μ; 1143–1255μ	3.519–863.9μ; 1143–1512μ	3.519–8.639μ; 1143–1512μ	0.721–409.6μ; 493.6–1255μ

EXAMPLE 13

Another continuous operation was conducted in a manner similar to that of Example 12. The feed solution was formed by dissolving 355 g (8.87 mols) in 3550 g of water. To this was added 560 g (4.37 mols) of 5,5-dimethylhydantoin. The concurrent feeds were adjusted to maintain the pH of the aqueous reaction mixture at 7.0±0.2. The temperature was maintained at 55° C. The total amount of bromine (Br₂) fed was 1359.4 g (8.50 mols). As in Example 12, ten fractions of the reaction mixture were collected. However, in this operation, the addition rates were adjusted such that the average residence time was approximately 1 hour per fraction. The total isolated yield of 1,3-dibromo-5,5-dimethylhydantoin was 88% based on 5,5-dimethylhydantoin used and 90% based on the added bromine. The 1,3-dibromo-5,5-dimethylhydantoin product was obtained as a white crystalline solid. Table 8 summarizes the average particle size data and product distribution data relating to the product formed in this reaction. Fractions 5–10 represent the particle size of the product as formed during steady-state operating conditions. As in Example 12, the product formed was bimodal. In Table 8 "n.d." indicates that the particle size determination for the larger particle sized fraction was not determined; the instrument used could not measure particles having a particle size greater than 2000 microns. The overall average particle size of the product was at least 455.5 microns.

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was 4.67 grams/minute via a Masterflex Easy-Load peristaltic pump. The reaction mixture was stirred at 400 rpm. The pH of the reaction was monitored by measuring the pH of the effluent using a pH meter, and the pH ranged from 6.06 to 6.36 during the reaction. Product removal from the reactor was also controlled by a pump. Residence time was, on average, 30 minutes per fraction; each fraction was about 500 mL. A yield of 90.5% of 1,3-dibromo-5,5-dimethylhydantoin was obtained, based on the amount of 5,5-dimethylhydantoin fed to the reactor. The active bromine content of the 1,3-dibromo-5,5-dimethylhydantoin was >55.3%, as determined by standard iodometric titration. Thus, the purity of this product was greater than 99.0%.

Table 9 summarizes particle size data on the 1,3-dibromo-5,5-dimethylhydantoin product formed in the continuous operation of Example 14. These data are averaged data based on two samples taken at different times during the continuous operation once steady state conditions, or essentially steady state conditions, had been achieved.

TABLE 9

Particle Size Category	Particle Size of Product
Average	188.9μ
10% is greater than	295.2μ
25% is greater than	255.6μ
50% is greater than	203.1μ
75% is greater than	122.5μ
90% is greater than	55.9μ
Range	0.872–356.5μ

TABLE 8

Particle Size	Fraction 5	Fraction 6	Fraction 7	Fraction 8	Fractions 9 + 10
Average	421.2μ	478.6μ	494.0μ	536.6μ	631.9μ
10% is greater than	606.5μ	699.3μ	781.7μ	1063μ	1438μ
25% is greater than	532.1μ	623.4μ	681.5μ	813.9μ	995.7μ
50% is greater than	452.3μ	535.0μ	548.5μ	546.7μ	522.8
75% is greater than	340.0μ	372.2μ	176.6μ	150.3μ	160.7μ
90% is greater than	140.8μ	112.8μ	68.94μ	72.93	81.68μ
Range	2.423–786.9μ; n.d.	2.423–863.9μ; n.d.	1.520–863.9μ; 1255–1512μ	0.04–2000μ; n.d.	0.04–>2000μ; n.d.

EXAMPLE 14

Another continuous operation was performed using a glass reactor into which were concurrently fed, on a continuous basis, an aqueous solution formed from 5,5-dimethylhydantoin and NaOH, and a separate feed of bromine. The aqueous solution was made by adding 5,5-dimethylhydantoin to an aqueous 9 wt % NaOH solution. This solution contained about 22.4 wt % of 5,5-dimethylhydantoin and 7 wt % NaOH. A one liter, jacketed reactor having an interior diameter of 82 millimeters equipped with an anchor agitator, with an outer diameter of 72 millimeters, was used, and a silicone fluid (Rhodersil 4720V20 fluid; Rhone-Poulenc) was circulated through the jacketing. The temperature of the reaction was controlled at 38° C. Both feeds were controlled by pumps; the average feed rate of the 5,5-dimethylhydantoin/NaOH solution was 15.84 grams/minute via a Prominent Gamma G/4A positive displacement pump, and the average feed rate of the bromine

Examples 15 and 16 illustrate methods of producing tablets from large average particle size 1,3-dibromo-5,5-dimethylhydantoin without use of binders, and the exceptional crush strength of such binder-free tablets. Example 17 illustrates the excellent flowability characteristics and low-dusting properties possessed by the large average particle size 1,3-dibromo-5,5-dimethylhydantoin.

EXAMPLE 15

Five gram samples of 1,3-dibromo-5,5-dimethylhydantoin produced by the process referred to

above were compacted without binder in a Sintech® press (MTS Systems Corporation, Edenprairie, Minn.) equipped with a punch and die fabricated from Hastelloy® C alloy. Prior to filling the die, the interior surfaces of the die were lightly dusted with a micronized polypropylene wax (MICROPRO 400 wax; Micro Powders, Incorporated, Tarrytown, N.Y.) to serve as a lubricant. The pressure applied was 5000 psi with no dwell time, i.e., the pressure was automatically terminated immediately upon reaching 5000 psi. The resultant tablets after removal from the die were aged for 6 days at room temperature. Thereupon the tablets were subjected to crush strength testing utilizing a Sintech® 1/S compression apparatus (MTS Systems Corporation, Edenprairie, Minn.) equipped with Testworks software, which software is installed in the 1/S compression apparatus as supplied by MTS Systems Corporation. The apparatus includes a horizontal circular-shaped load cell interfaced with a computer, a digital micrometer also interfaced with the computer, and a vertical screw-driven piston that is disposed above the load cell and adapted to apply a downward force perpendicular to the load cell. The procedure for measuring crush strength involves measuring the thickness of the tablet with the micrometer to provide a digitized input to the computer. Next the tablet is placed on its edge on the load cell with the piston in contact with the upper edge of the tablet. Then the apparatus is activated whereby the piston commences applying a progressively increasing downward diametral force to the tablet. At the same time, the load cell continuously measures the downward force being applied to the tablet, and the input of such measurements is transmitted to the computer. When the force being applied reaches the point where the amount of force suddenly decreases to 10% of the immediately preceding force, the tablet has reached the breaking point, and the application of the force is immediately terminated by the software program. From the inputs to the computer, two values are provided, namely the pounds of force at the breaking point of the tablet, and the pounds of force per inch thickness of the tablet at the breaking point. Thus the greater the force applied, the greater the strength. Two groups of such tests were conducted. One set (Set A) involved forming and evaluating 5 tablets from a batch of 1,3-dibromo-5,5-dimethylhydantoin produced in a continuous process described in Example 13. The other set (Set B) of tests involved 3 tablets produced from another batch of 1,3-dibromo-5,5-dimethylhydantoin produced in a batch process of the type described in Example 9. Table 10 summarizes the results of these tests.

TABLE 10

Test Set	Tablet Thickness	Crush Strength	Crush Strength
A	0.365 in.	20.9 lb.	57.3 lb./in.
A	0.367 in.	25.5 lb.	69.5 lb./in.
A	0.366 in.	19.2 lb.	52.5 lb./in.
A	0.367 in.	22.8 lb.	62.1 lb./in.
A	0.364 in.	23.7 lb.	65.0 lb./in.
Avg. of A		22.4 lb.	61.3 lb./in.
B	0.353 in.	10.7 lb.	30.4 lb./in.
B	0.352 in.	12.8 lb.	36.4 lb./in.
B	0.354 in.	9.8 lb.	27.8 lb./in.
Avg. of B	—	11.1 lb.	31.5 lb./in.

Tablets of conventional, small particle sized 1,3-dibromo-5,5-dimethylhydantoin devoid of binder cannot be tableted in the manner described above.

EXAMPLE 16

The crush strength of tablets formed from 1,3-dibromo-5,5-dimethylhydantoin formulated with a binder was illus-

trated in a group of tests conducted as described in Example 15. The procedure for producing the tablets was as follows: 1,3-dibromo-5,5-dimethylhydantoin produced as in Example 14 was hand-mixed with 3% by weight of micronized polyethylene wax from Micro Powders Incorporated, Tarrytown, N.Y. for approximately 30 minutes. The resultant formulation was then converted into tablets as described in Example 15. The results of the crush strength tests, conducted as described in Example 15, are summarized in Table 11.

TABLE 11

Tablet Thickness	Crush Strength	Crush Strength
0.372 in.	39.8 lb.	107.2 lb./in.
0.375 in.	44.9 lb.	119.9 lb./in.
0.375 in.	37.5 lb.	1000 lb./in.
0.375 in.	36.1 lb.	96.5 lb./in.
0.377 in.	37.6 lb.	99.7 lb./in.
Averaged Results	39.2 lb.	104.6 lb./in.

EXAMPLE 17

Comparative flowability tests were carried out using a sample of 1,3-dibromo-5,5-dimethylhydantoin and samples of commercially-available 1,3-dihalo-5,5-dimethylhydantoin products. These tests involved filling an 8-ounce glass jar to about one-third of its capacity with the sample to be tested. After closing the jar, it was slowly rotated while on its side in a single direction while observing the characteristics of the contents. In Table 14 the following abbreviations are used:

DBDMH is 1,3-dibromo-5,5-dimethylhydantoin
DCDMH is 1,3-dichloro-5,5-dimethylhydantoin
BCDMH is N,N'-bromochloro-5,5-dimethylhydantoin

TABLE 12

N,N'-dihalohydantoin	Average Particle Size	Source	Product Characteristics
DCDMH	108.1 microns	Aldrich Chemical Co.	Bridging occurred; high dusting, non-free-flowing product
BCDMH	323.8 microns	Aldrich Chemical Co.	Bridging occurred; high dusting, non-free-flowing product
DBDMH	162.1 microns	Aldrich Chemical Co.	Bridging occurred; high dusting, non-free-flowing product
DBDMH	64.5 microns	Albemarle Corporation	Bridging occurred; high dusting, non-free-flowing product
DBDMH	45.2 microns	Great Lakes Chemical Corporation	Bridging occurred; high dusting, non-free-flowing product
DBDMH	293.6 microns	The new process of application Ser. No. 09/484,844	No bridging occurred; low dusting, free-flowing powder

Examples 18–26 illustrate the preparation and properties of compacted products formed from 1,3-dibromo-5,5-dimethylhydantoin utilizing novel binders as described in commonly-owned copending application Ser. No. 09/487,816, filed Jan. 18, 2000.

EXAMPLE 18

2.5 Grams of a micronized polyethylene wax (MPP-611, Micro Powders Inc., Tarrytown, N.Y.), was weighed into a

crystallizing dish, followed by 1,3-dibromo-5,5-dimethylhydantoin (47.5 g). A broad-bladed spatula was used to blend the mixture rather like a cook might blend butter into flour. After 10 minutes of hand mixing in this fashion, the product was admitted to a glass bottle which was rolled to assess the flowability of the mixture. The flow properties were improved over the properties of the 1,3-dibromo-5,5-dimethylhydantoin used to make the blend.

EXAMPLE 19

2.5 Grams of polypropylene wax (MICROPRO 400, Micro Powders Inc., Tarrytown, N.Y.), was weighed into a crystallizing dish, followed by 1,3-dibromo-5,5-dimethylhydantoin (47.5 g). This mixture was blended as described in Example 18, and transferred to a glass bottle which was rolled to assess the flowability of the blend. Its flow properties were improved over the properties of the 1,3-dibromo-5,5-dimethylhydantoin used to make the blend.

EXAMPLE 20

The 1,3-dibromo-5,5-dimethylhydantoin blends prepared in Examples 18 and 19 were subjected to a compaction test. Each sample was weighed, and introduced into a 0.71 inch diameter die made from Hastelloy® C alloy and compacted with a screw-driven punch, also made of Hastelloy® C alloy, to a pre-set pressure. Before filling the die, its interior surfaces were lightly dusted with micronized polypropylene wax to serve as a lubricant. There was no dwell time upon attaining the compaction pressure (the pressure was released immediately). Upon extracting the tablet from the die, the thickness of the tablet was measured with a micrometer, and a visual observation of the tablet was made.

For comparison, the blends were compared to unblended, virgin, commercially produced 1,3-dibromo-5,5-dimethylhydantoin powder with an average particle size of about 64.5µ, and a commercial toilet bowl product (abbreviated in Table 13 as CTB product), which is known to be a mixture of other halogenated hydantoin compounds. This toilet bowl puck was purchased from a supermarket and ground to a powder with a mortar and pestle, and recompacted as above described.

Table 13 lists the experimental conditions and the observations.

TABLE 13

Blend	Amount of blend added to die	Pressure	Tablet thickness	Observations
DBDMH/5 wt % MPP-611	5.0 g	5000 psi	0.389 in.	Intact tablet, smooth shiny surfaces
DBDMH/5 wt % Micropro 400	5.0 g	5000 psi	0.374 in.	Intact tablet, not 100% mold release from top punch
DBDMH	2.5 g	5000 psi	—	compact shattered and laminated on removal from die
CTB product	2.5 g	5000 psi	0.22 in.	Intact tablet

EXAMPLE 21

The 1,3-dibromo-5,5-dimethylhydantoin/5 wt % MPP-611 tablets produced in Example 19 were placed in glass beakers of water. The tablet appeared to do nothing. Its

physical integrity remained intact as it slowly dissolved over a period of several months. In order to prove that it was releasing dissolved halogen, the tablet was removed from the water, washed with deionized water and dried with a paper towel. A plastic wash bottle was then used to wash the tablet into a deionized water solution containing N,N-diethyl-phenylenediamine (DPD) powder. This solution immediately turned pink when the wash pressure on the tablet until it breaks. The pressure required to reach the breaking point is recorded and reported as the crush strength.

The crush strength of the tablets was compared to a commercial toilet bowl product (abbreviated as CTB product in Table 15). This was purchased from a supermarket, ground to a powder and re-compacted under the conditions described above.

Table 15 summarizes the observations and results. The crush strength data represent an average of 3 separate measurements.

TABLE 15

Blend	Average thickness	Average crush strength	Observations
DBDMH/5 wt % MPP-611	0.38 in.	93.7 lb./in.*	Single tablets, shiny surfaces, low dust
DBDMH/3 wt % MPP-611	0.38 in.	57.9 lb./in.	Single tablets, shiny surfaces, low dust
DBDMH/2 wt % MPP-611	0.37 in.	37.0 lb./in.	Single tablets, shiny surface, low dust
CTB product	0.44 in.	55.2 lb./in.	Single tablets, dull surfaces, dusty

*An estimate because 2 of the 3 tablets did not break before the limit of the load cell was exceeded.

The data in Table 15 clearly demonstrate that the crush strength of the tablets is a function of the micronized polyethylene wax loading, and that when using micronized polyethylene wax with 1,3-dibromo-5,5-dimethylhydantoin, it is possible to obtain a stronger product than a commercial toilet bowl product.

EXAMPLE 22

1,3-Dibromo-5,5-dimethylhydantoin was blended with micronized polyethylene wax (MPP-611) such that the blend contained 3 wt % of the wax. A sample of the blend (5 g) was introduced to a die made from Hastelloy® C alloy, and compacted to a pressure of 5000 psi. Three more samples (5 g each) were compacted in the same manner, and each time a single tablet was extracted from the die after the pressure had been released. In each case, before filling the die, its interior surfaces were lightly dusted with micronized polypropylene wax to serve as a lubricant. The tablets were manually broken into two equally-sized pieces. One half of each tablet was crushed into a powder with a mortar and pestle, and the powder was titrated to determine its wt % of active bromine. The other half of each tablet was placed in a sealed glass vial and placed in an oven at 50° C. After 30 days, the samples were removed from the oven, ground up, and titrated to determine its wt % of active bromine. For comparative purposes, a control sample of commercially produced 1,3-dibromo-5,5-dimethylhydantoin having an average particle size of about 64.5µ (containing no micronized polyethylene wax) was subjected to the same operations. In the case of this control sample, it was not possible to extract a single tablet from the die, and thus only shattered laminates could be tested.

Table 14 lists the results obtained for four samples of 1,3-dibromo-5,5-dimethylhydantoin/3 wt % micronized

polyethylene wax blends, along with the control sample
containing no additive.

TABLE 14

	Wt % Active Bromine	
	Initial	After 30 days
Sample 1	53.4	53.3
Sample 2	53.3	53.6
Sample 3	54.2	53.3
Sample 4	53.3	53.7
Control	55.3	55.2

The data in Table 14 indicate that, within the reproduc-
ibility of the analytical technique used, the presence of 3 wt
% of micronized polyethylene wax in a 1,3-dibromo-5,5-
dimethylhydantoin tablet does not induce a loss of active
bromine after storage at 50° C. for 30 days. This absence of
active bromine loss demonstrates the chemical compatibility
of 1,3-dibromo-5,5-dimethylhydantoin and micronized
polyethylene wax.

EXAMPLE 23

The strength of 1,3-dibromo-5,5-dimethylhydantoin
tableted with different amounts of micronized polyethylene
wax, as described in Example 22, was measured in a series
of crush strength tests. In each test, 5 g of blended material
was added to a die made from Hastelloy® C alloy and
compressed with a screw-driven punch, also made from
Hastelloy C alloy, to a pressure of 5000 psi. In each case,
before filling the die, the interior surfaces of the die were
lightly dusted with micronized polypropylene wax to serve
as a lubricant. After extraction of the tablet from the die, a
visual observation of the tablet was made.

A Sintech® 1/S compression apparatus equipped with
Testworks software was used to determine the crush strength
of the tablets. This uses a screw-driven piston to exert
dibromo-5,5-dimethylhydantoin having an average particle
size of about 64.5μ. Tableting and crush strength testing
were performed as described in Examples 22 and 23.

The crush strength of the tablets was compared to a
commercial toilet bowl product (abbreviated as CTB prod-
uct in Table 16). This commercial toilet bowl product was
purchased from a supermarket, ground to a powder, and
re-tableted under the conditions described in Example 22.

Table 16 summarizes the observations and results. The
crush strength data represent an average of 3 separate
measurements.

TABLE 16

DBDMH blend	Average thickness	Average crush strength	Observations
Polyfluo 200 wax	0.38 in.	30.2 lb/in.	Single tablets, tend to end-cap on breaking
Polyfluo 400 wax	0.37 in.	22.2 lb/in.	Single tablets, tend to end-cap on breaking
Micropro 400 wax	0.36 in.	11.8 lb/in.	Single tablets, tend to end-cap on breaking
Synfluo 180 VF	0.38 in.	37.8 lb/in.	Single tablets, tend to end-cap on breaking
Polysilk 600	—	—	Powder is discolored, chemical incompatibility; no tablets were made

TABLE 16-continued

DBDMH blend	Average thickness	Average crush strength	Observations
Handy Tack 140 resin	0.39 in.	27.5 lb/in.	Tablets are discolored, chemical incompatibility
CTB product	0.44 in.	102.3 lb/in.	Single tablets

Although in the tests summarized in Table 16 the 1,3-
dibromo-5,5-dimethylhydantoin tablets were not as strong
as the prepared sample of CTB product, nevertheless all of
the micronized waxes served as effective binders for 1,3-
dibromo-5,5-dimethylhydantoin in that they produced
whole tablets that remained intact when extracted from a die,
and that exhibited adequate crush strength. However, a
micronized modified petroleum resin (Handy Tack 140,
Micro Powders Inc., Tarrytown, N.Y.) and a fluorinated
hydrocarbon mixture (Polysilk 600, Micro Powders Inc.,
Tarrytown, N.Y.) both displayed signs of chemical incom-
patibility with 1,3-dibromo-5,5-dimethylhydantoin.

EXAMPLE 24

A series of different blends was prepared using a variety
of micronized waxes (purchased from Micro Powders
Incorporated, Tarrytown, N.Y.). Each blend was prepared in
the fashion described in Example 18, such that the blend
contained 3 wt % wax. The source of the DBDMH used in
forming these blends was commercially produced 1,3-water
was introduced, proving that soluble halogen was being
washed from the tablet. In this connection, DPD is an
indicator of high sensitivity used to detect the presence of
soluble halogen at the parts per million level. In the presence
of such quantities of dissolved halogen, the DPD turns pink.

EXAMPLE 25

Blending and tableting studies were scaled up. A ribbon
blender with a volume of two cubic feet was used to mix 25
kg of commercially produced 1,3-dibromo-5,5-
dimethylhydantoin, having an average particle size of about
64.5μ, with micronized polyethylene wax (MPP-611) to
achieve loadings of 2.0 wt % and 5 wt % of wax. The
mixing time was 60 minutes in each case. A double-cone,
tumble blender with a volume of 5 cubic feet was used to
tumble mix 25 kg of 1,3-dibromo-5,5-dimethylhydantoin
with micronized polyethylene wax to achieve a loading of 3
wt % of wax. The mixing time was 240 minutes.

Each blend was passed through a Chilsonator® breaker
(The Fitzpatrick Company, Elmhurst, Ill.) and a set of
screens to produce compacted granules of U.S. mesh size 12
to 18. Virgin, commercially-produced 1,3-dibromo-5,5-
dimethylhydantoin having an average particle size of about
64.5μ, without micronized polyethylene wax, was also
passed through the same equipment. This material did not
compact and form granules. Instead, material exiting the
Chilsonator® was mostly loose powder.

The granules of each 1,3-dibromo-5,5-
dimethylhydantoin/micronized polyethylene wax blend
were introduced to the feed hopper of a rotary tablet press.
The turret contained 18 die cavities, each of which is 0.75
inches in diameter, which was automatically filled with
granules and compressed between two punches made of
Hastelloy® C alloy. The tablets ejected from the tablet press
were collected, and 7 days later were subject to crush
strength testing. The results given in Table 17 are an average
of at least 3 tests.

TABLE 17

DBDMH Blend	Tablet Thickness	Crush strength
2 wt % MPP-611, tumble blender	0.49 in.	16.6 lb/in
2.5 wt % MPP-611, Ribbon blender	0.49 in.	19.3 lb/in
3 wt % MPP-611, Ribbon blender	0.72 in.	24.1 lb/in

The main findings from the runs of Example 25 were that the commercially produced 1,3-dibromo-5,5-dimethylhydantoin with an average particle size of about 64.5μ alone cannot be compacted into granules suitable for making tablets, and that the presence of micronized polyethylene wax (MPP-611) with such finely-divided 1,3-dibromo-5,5-dimethylhydantoin promotes the process of compaction into granules. These granules can be fed to a tableting machine and compacted into tablets. The strength of the tablets is governed by the amount of micronized polyethylene wax present. The higher the level of micronized polyethylene wax, the stronger the tablet.

EXAMPLE 26

The crush strength of tablets formed from a large average particle sized 1,3-dibromo-5,5-dimethylhydantoin formulated with a binder was measured. This 1,3-dibromo-5,5-dimethylhydantoin had an average particle size of about 189 microns, and the binder was a micronized polyethylene wax (MPP-611), and the binder was 3 wt % of the blend. The measurements were made utilizing a Sintech 1/S compression apparatus equipped with Testworks software. In these tests the tablets were subjected to increasing force applied along the longitudinal axis of the tablet until breakage occurred. The procedure for producing the tablets was as described in Example 21. The results of the crush strength tests are summarized in Table 18.

TABLE 18

Tablet Thickness	Crush Strength	Crush Strength
0.372 in.	39.8 lb.	107.2 lb./in.
0.375 in.	44.9 lb.	119.9 lb./in.
0.375 in.	37.5 lb.	100.0 lb./in.
0.375 in.	36.1 lb.	96.5 lb./in.
0.377 in.	37.6 lb.	99.7 lb./in.
Averaged Results	39.2 lb.	104.6 lb./in.

As can be seen from the foregoing description, there are a great number of important ways of carrying out or implementing this invention. In brief summary, some of these embodiments are as follows:

A) A method of effecting microbiocidal activity in a body of water, which method comprises providing in such body of water using a 1,3-dibromo-5,5-dialkylhydantoin microbiocidal agent described herein (DBDAH), most preferably 1,3-dibromo-5,5-dimethylhydantoin (DBDMH), a concentration of "free chlorine" that is greater than could be predicted from the concentration of "free chlorine" provided by an equimolar amount of N,N'-bromochloro-5,5-dimethylhydantoin (BCDMH), as determinable by Hach Method 8021 (copyright 1997, by Hach Company) and for "total chlorine" using Hach Method 8167 (copyright 1997, by Hach Company), and converting the mg/L Cl₂ "free chlorine" values from the tests to percentages of the mg/L Cl₂ "total chlorine" values from the tests, the four water samples used in said tests

each having the same pH as said body of water and containing an equimolar quantity of BCDMH or DBDAH.

B) A method of A) above wherein the molar amount of the 1,3-dibromo-5,5-dialkylhydantoin microbiocidal agent (DBDAH), most preferably 1,3-dibromo-5,5-dimethylhydantoin, provided in said body of water is less than the molar amount of N,N'-bromochloro-5,5-dimethylhydantoin required to achieve the same degree of microbiological control.

C) Individual methods of A) or B) above wherein the 1,3-dibromo-5,5-dialkylhydantoin microbiocidal agent (DBDAH) used is 1,3-dibromo-5,5-dimethylhydantoin having (a) an average particle size in the range of about 20 to about 600 microns, (b) an average particle size of at least about 175 microns, (c) an average particle size of at least about 200 microns, (d) an average particle size of at least about 300 microns, or (e) an average particle size of at least about 400 microns.

D) Individual methods of A) or B) above wherein the 1,3-dibromo-5,5-dialkylhydantoin microbiocidal agent (DBDAH) used is (i) 1,3-dibromo-5,5-dimethylhydantoin in the form of a compacted product produced without a binder, or (ii) at least one 1,3-dibromo-5,5-dialkylhydantoin microbiocidal agent described herein (DBDAH), most preferably 1,3-dibromo-5,5-dimethylhydantoin, in the form of a compacted product produced using as a binder an amount of a micronized synthetic polyolefin-based hydrocarbon wax and/or a micronized synthetic polyfluorocarbon wax effective to form the compacted product, the wax being compatible with the 1,3-dibromo-5,5-dialkylhydantoin, or (iii) in the form of a compacted product formed from at least one 1,3-dibromo-5,5-dialkylhydantoin microbiocidal agent described herein (DBDAH), most preferably 1,3-dibromo-5,5-dimethylhydantoin, wherein the compacted product was produced using as a binder an amount of a saturated, normally solid, fatty amide effective to form the compacted product.

E) Individual methods of (i) of D) above wherein the 1,3-dibromo-5,5-dimethylhydantoin being used has an average particle size of at least about 175, at least about 200, at least about 300, or at least about 400, microns.

F) Individual methods of (ii) of D) above wherein the wax is micronized polyethylene wax having, prior to compaction, an average particle size of no greater than about 15 microns, a maximum particle size of no greater than about 40 microns, and a density in the range of about 0.9 to about 1.4 grams per cc at 25° C.; or a micronized polyethylene wax that, prior to compaction, melts at a temperature in the range of about 109° C. to about 111° C.; or a micronized polypropylene wax having, prior to compaction, an average particle size in the range of about 5.0 to about 7.0 microns, a maximum particle size of about 22 microns, and a density in the range of about 0.9 to about 1.4 grams per cc at 25° C.; a micronized polypropylene wax that melts at a temperature in the range of about 140° C. to about 143° C., that has an average particle size in the range of about 5.0 to about 7.0 microns, and that has a maximum particle size of about 22 microns.

G) Individual methods of (iii) of D) above wherein the 1,3-dibromo-5,5-dialkylhydantoin being used is 1,3-dibromo-5,5-dimethylhydantoin having an average particle size of at least about 200, at least about 300, at least about 400, or at least about 500, microns.

H) Individual methods of A) or B) above wherein the microbiocidal activity in said body of water comprises combating *Escherichia coli* and/or *Enterococcus faecium* in said body of water.

I) A method of purveying a microbiological control agent for use in water in accordance with U.S. Environmental Protection Agency regulations, which method comprises purveying a container of a water control agent comprising at least one 1,3-dibromo-5,5-dialkylhydantoin microbiocidal agent described herein (DBDAH), most preferably 1,3-dibromo-5,5-dimethylhydantoin, the container bearing a label having thereon dosage levels pursuant to requirements promulgated by the U.S. Environmental Protection Agency, and specifying either on said label, or on or in packaging for said container, to the effect that the contents are recommended for use, or are for use, in water treatment, or to the effect that the contents are recommended for use, or are for use, in water having a pH of at least about 8.0.

J) Individual methods of H) or I) above wherein the 1,3-dibromo-5,5-dialkylhydantoin being used in H) or the control agent being used in I) is (i) 1,3-dibromo-5,5-dimethylhydantoin in the form of a compacted product produced without a binder, (ii) at least one 1,3-dibromo-5,5-dialkylhydantoin microbiocidal agent described herein (DBDAH), most preferably 1,3-dibromo-5,5-dimethylhydantoin, in the form of a compacted product produced using as a binder an amount of a micronized synthetic polyolefin-based hydrocarbon wax and/or a micronized synthetic polyfluorocarbon wax effective to form the compacted product, the wax being compatible with the 1,3-dibromo-5,5-dialkylhydantoin, or (iii) at least one 1,3-dibromo-5,5-dialkylhydantoin microbiocidal agent described herein (DBDAH), most preferably 1,3-dibromo-5,5-dimethylhydantoin, in the form of a compacted product formed from the 1,3-dibromo-5,5-dialkylhydantoin wherein the compacted product was produced using as a binder an amount of a saturated, normally solid, fatty amide effective to form the compacted product.

K) Individual methods of (i) of J) above wherein the 1,3-dibromo-5,5-dimethylhydantoin being used has an average particle size of at least about 175, at least about 200, at least about 300, or at least about 400, microns.

L) Individual methods of (ii) of J) above wherein the wax is polyethylene wax having, prior to compaction, an average particle size of no greater than about 15 microns, a maximum particle size of no greater than about 40 microns, and a density in the range of about 0.9 to about 1.4 grams per cc at 25° C.; or wherein the wax is a polyethylene wax that, prior to compaction, melts at a temperature in the range of about 109° C. to about 111° C.; or wherein the wax is polypropylene wax having, prior to compaction, an average particle size in the range of about 5.0 to about 7.0 microns, a maximum particle size of about 22 microns, and a density in the range of about 0.9 to about 1.4 grams per cc at 25° C.; or wherein the wax, prior to compaction, is a polypropylene wax that melts at a temperature in the range of about 140° C. to about 143° C., that has an average particle size in the range of about 5.0 to about 7.0 microns, and that has a maximum particle size of about 22 microns.

M) Individual methods of (iii) of J) above wherein the 1,3-dibromo-5,5-dialkylhydantoin used in forming the

compacted product is 1,3-dibromo-5,5-dimethylhydantoin having an average particle size of at least about 200, at least about 300, or at least about 400, microns.

N) Individual methods of any of A)–M) above wherein the body of water being treated is industrial cooling water, wastewater, or process water.

O) A method of N) above wherein the treatment of the water comprises passing a sidestream of the water through a bed of the 1,3-dibromo-5,5-dialkylhydantoin such that a biocidally effective amount of the 1,3-dibromo-5,5-dialkylhydantoin is delivered to the water.

P) Individual methods of I) above wherein the microbiological control agent is purveyed for use in at least cooling water, wastewater, or process water.

Q) Individual methods of A) or B) above wherein the microbiocidal activity in said body of water comprises eradicating, substantially eradicating, or reducing biofilm on a surface in contact with said body of water.

R) Individual methods of Q) above wherein the 1,3-dibromo-5,5-dialkylhydantoin being used is (i) 1,3-dibromo-5,5-dimethylhydantoin having (a) an average particle size in the range of about 20 to about 600 microns, (b) an average particle size of at least about 175 microns, (c) an average particle size of at least about 200 microns, (d) an average particle size of at least about 300 microns, or (e) an average particle size of at least about 400 microns.

S) Individual methods of Q) above wherein the 1,3-dibromo-5,5-dialkylhydantoin being used is (i) 1,3-dibromo-5,5-dimethylhydantoin in the form of a compacted product produced without a binder, or (ii) at least one 1,3-dibromo-5,5-dialkylhydantoin described herein (DBDAH), most preferably 1,3-dibromo-5,5-dimethylhydantoin, in the form of a compacted product produced using as a binder an amount of a micronized synthetic polyolefin-based hydrocarbon wax and/or a micronized synthetic polyfluorocarbon wax effective to form the compacted product, the wax being compatible with the 1,3-dibromo-5,5-dialkylhydantoin, or (iii) at least one 1,3-dibromo-5,5-dialkylhydantoin described herein (DBDAH), most preferably 1,3-dibromo-5,5-dimethylhydantoin, in the form of a compacted product formed from the 1,3-dibromo-5,5-dialkylhydantoin wherein the compacted product was produced using as a binder an amount of a saturated, normally solid, fatty amide effective to form the compacted product.

T) Individual methods of (i) of S) above wherein the 1,3-dibromo-5,5-dimethylhydantoin being used has an average particle size of at least about 175, at least about 200, at least about 300, or at least about 400, microns.

U) Individual methods of (ii) of S) above wherein the wax is micronized polyethylene wax having, prior to compaction, an average particle size of no greater than about 15 microns, a maximum particle size of no greater than about 40 microns, and a density in the range of about 0.9 to about 1.4 grams per cc at 25° C.; or a micronized polyethylene wax that, prior to compaction, melts at a temperature in the range of about 109° C. to about 111° C.; or a micronized polypropylene wax having, prior to compaction, an average particle size in the range of about 5.0 to about 7.0 microns, a maximum particle size of about 22 microns, and a density in the range of about 0.9 to about 1.4 grams per cc at 25° C.; a micronized polypropylene wax that melts at a temperature in the range of about

140° C. to about 143° C., that has an average particle size in the range of about 5.0 to about 7.0 microns, and that has a maximum particle size of about 22 microns.

V) Individual methods of (iii) of S) above wherein the 1,3-dibromo-5,5-dialkylhydantoin being used is 1,3-dibromo-5,5-dimethylhydantoin having an average particle size of at least about 200, at least about 300, at least about 400, or at least about 500, microns.

W) Individual methods of A) or B) above wherein the microbiocidal activity in said body of water comprises eradicating, substantially eradicating, or at least reducing *Pseudomonas aeruginosa* biofilm on a surface in contact with said body of water.

X) A method of purveying a biofilm control agent for use in water in accordance with U. S. Environmental Protection Agency regulations, which method comprises purveying a container of a biofilm control agent for use in aqueous media, such agent comprising at least one 1,3-dibromo-5,5-dialkylhydantoin described herein (DBDAH), most preferably 1,3-dibromo-5,5-dimethylhydantoin, the container bearing a label having thereon dosage levels pursuant to requirements promulgated by the U.S. Environmental Protection Agency, and specifying either on said label, or on or in packaging for said container, to the effect that the contents are recommended for use, or are for use, with water having a pH of at least about 8.0.

References herein to biofilm on a surface in contact with an aqueous medium or water, are not to be construed as requiring the aqueous medium or water to be in constant contact with such surface. As long as the aqueous medium or water comes into contact with a surface often enough to result in the formation of biofilm on such surface, it is within the scope of this invention to treat such aqueous medium or water pursuant to this invention so as to combat such biofilm. For example, this invention includes treatment of aqueous media or water that is splashed, sprayed, or dripped on or against a surface with sufficient frequency for biofilm to develop on such surface. It is also to be understood that the aqueous medium or the water can contain any of a variety of contaminants and/or impurities. The only requirements are that such aqueous medium or water periodically or constantly contacts a surface such that the formation of biofilm occurs on the surface, and that the contaminants and/or impurities in the aqueous medium or water do not prevent the 1,3-dibromo-5,5-dialkylhydantoin(s) such as 1,3-dibromo-5,5-dimethylhydantoin, from eradicating, or at least reducing the amount of, the biofilm on such surface.

As used herein, including the claims, the term "purveying" means carrying out or causing to be carried out one or more of the following activities: advertising, marketing, promoting for sale, offering for sale, selling, bartering, trading, leasing, merchandising, importing, exporting, dealing in commerce with, supplying, distributing, delivering, and any and all other activities of similar import.

As used herein, including the claims, the terms "aqueous medium" and "water" refer to and include any liquid in which the predominate liquid component is water. Such aqueous medium or water may contain various other materials, whether organic or inorganic, or both, and is exemplified by recreational water, industrial cooling water, process water and wastewater. As is well known in the art, if the water has a pH of at least about 8, it is not included in the category of recreational water, at least at the present time in the United States.

Compounds referred to by chemical name or formula anywhere in this document, whether referred to in the

singular or plural, are identified as they exist prior to coming into contact with another substance referred to by chemical name or chemical type (e.g., another component, a solvent, or etc.). It matters not what preliminary chemical changes, if any, take place in the resulting mixture or solution, as such changes are the natural result of bringing the specified substances together under the conditions called for pursuant to this disclosure. Also, even though the claims may refer to substances in the present tense (e.g., "comprises", "is", etc.), the reference is to the substance as it exists at the time just before it is first contacted, blended or mixed with one or more other substances in accordance with the present disclosure.

Except as may be expressly otherwise indicated, the article "a" or "an" if and as used herein is not intended to limit, and should not be construed as limiting, a claim to a single element to which the article refers. Rather, the article "a" or "an" if and as used herein is intended to cover one or more such elements, unless the text expressly indicates otherwise.

It will also be understood that the terms "substantial" and "substantially" denote that chemical operations or treatments ordinarily do not involve absolutes. Thus instead of describing a variable or a result as an absolute, it is far more realistic to describe the variable or result as being in the substantial vicinity of the expressed variable or result. For example when describing eradication of an organism, it can be more realistic to refer to the substantial eradication of the organism rather than to imply that absolute total eradication occurs, since one skilled in the art fully realizes that a substantial kill is a very desirable result, and the possibility always exists that even if a small portion of the organism survives the treatment, the overall result is nevertheless highly beneficial in most cases. Thus this document should be read with the application of common sense.

Each and every patent, publication, or commonly-owned patent application referred to in any portion of this specification is incorporated in toto into this disclosure by reference, as if fully set forth herein.

This invention is susceptible to considerable variation in its practice. Therefore the foregoing description is not intended to limit, and should not be construed as limiting, the invention to the particular exemplifications presented hereinabove. Rather, what is intended to be covered is as set forth in the ensuing claims and the equivalents thereof permitted as a matter of law.

That which is claimed is:

1. A method of providing microbiological control in an aqueous medium and/or eradication or reduction of biofilm on a surface in contact with such aqueous medium, which method comprises introducing into the aqueous medium a microbiocidally effective amount of at least one 1,3-dibromo-5,5-dialkylhydantoin in which one of the alkyl groups in the 5-position is a methyl group and in which the other alkyl group in the 5-position has in the range of 1 to 4 carbon atoms, wherein (i) the molar quantity of said at least one 1,3-dibromo-5,5-dialkylhydantoin introduced into said aqueous medium is less than the molar quantity of N,N'-bromochloro-5,5-dimethylhydantoin that would be required to effect the same degree of microbiological control in said medium, (ii) the quantity of said at least one 1,3-dibromo-5,5-dialkylhydantoin introduced into said aqueous medium releases an amount of "free chlorine" that is greater than the amount of "free chlorine" that would be released in said medium by an equimolar quantity of N,N'-bromochloro-5,5-dimethylhydantoin, and (iii) the amount of "free chlorine" released by the quantity of said at least one

1,3-dibromo-5,5-dialkylhydantoin introduced into said medium is greater than the amount of "free chlorine" that could be predicted to be released by that quantity of said at least one 1,3-dibromo-5,5-dialkylhydantoin on the basis of the amount of "free chlorine" that would be released in said medium by an equimolar quantity of N,N'-bromochloro-5, 5-dimethylhydantoin.

2. A method of claim 1 wherein said at least one 1,3-dibromo-5,5-dialkylhydantoin is 1,3-dibromo-5-isobutyl-5-methylhydantoin.

3. A method of claim 1 wherein said at least one 1,3-dibromo-5,5-dialkylhydantoin is 1,3-dibromo-5-n-propyl-5-methylhydantoin.

4. A method of claim 1 wherein said at least one 1,3-dibromo-5,5-dialkylhydantoin is 1,3-dibromo-5-ethyl-5-methylhydantoin.

5. A method of claim 1 wherein said at least one 1,3-dibromo-5,5-dialkylhydantoin is a mixture of two or more of said 1,3-dibromo-5,5-dialkylhydantoins.

6. A method of claim 1 wherein said at least one 1,3-dibromo-5,5-dialkylhydantoin is a mixture of 1,3-dibromo-5,5-dimethylhydantoin and 1,3-dibromo-5-ethyl-5-methylhydantoin.

7. A method of claim 1 wherein said aqueous medium has a pH of at least about 8.0.

8. A method of providing microbiological control in an aqueous medium having a pH of at least about 8.0 and/or eradication or reduction of biofilm on a surface in contact with such aqueous medium, which method comprises introducing a microbiocidally effective amount of 1,3-dibromo-5,5-dimethylhydantoin into the aqueous medium, wherein (i) the quantity by weight of 1,3-dibromo-5,5-dimethylhydantoin introduced into the aqueous medium is less than the quantity by weight of N,N'-bromochloro-5,5-dimethylhydantoin that would be required to effect the same degree of microbiological control in said medium, (ii) the quantity of 1,3-dibromo-5,5-dimethylhydantoin introduced into the aqueous medium releases an amount of "free chlorine" that is greater than the amount of "free chlorine" that would be released in said medium by an equimolar quantity of N,N'-bromochloro-5,5-dimethylhydantoin, and (iii) the amount of "free chlorine" released by the quantity of the 1,3-dibromo-5,5-dimethylhydantoin introduced into said medium is greater than the amount of "free chlorine" that could be predicted to be released by that quantity of 1,3-dibromo-5,5-dimethylhydantoin on the basis of the amount of "free chlorine" that would be released in said medium by an equimolar quantity of N,N'-bromochloro-5,5-dimethylhydantoin.

9. A method of claim 8 wherein the 1,3-dibromo-5,5-dimethylhydantoin being used has an average particle size of at least about 175 microns.

10. A method of claim 8 wherein the 1,3-dibromo-5,5-dimethylhydantoin being used has an average particle size of at least about 200 microns.

11. A method of claim 8 wherein the 1,3-dibromo-5,5-dimethylhydantoin being used has an average particle size of at least about 300 microns.

12. A method of claim 8 wherein the 1,3-dibromo-5,5-dimethylhydantoin being used is in the form of a shape-retentive pressure compacted article produced by pressure compacting 1,3-dibromo-5,5-dimethylhydantoin particulate solids without use of a binder and without prior treatment of such solids to enhance their compactibility.

13. A method of claim 12 wherein the 1,3-dibromo-5,5-dimethylhydantoin particulate solids used in forming said article had, prior to compaction, an average particle size of at least about 175 microns.

14. A method of claim 8 wherein the 1,3-dibromo-5,5-dimethylhydantoin being used is in the form of a shape-retentive pressure compacted article produced by pressure compacting 1,3-dibromo-5,5-dimethylhydantoin particulate solids with use of a binder.

15. A method of claim 14 wherein the 1,3-dibromo-5,5-dimethylhydantoin particulate solids used in forming said article had, prior to compaction, an average particle size of at least about 175 microns.

16. A method of claim 8 wherein the 1,3-dibromo-5,5-dimethylhydantoin being used is in the form of a compacted product produced using as a binder an amount of a micronized synthetic polyolefin-based hydrocarbon wax and/or a micronized synthetic polyfluorocarbon wax effective to form said compacted product, said wax being compatible with said 1,3-dibromo-5,5-dimethylhydantoin.

17. A method of claim 16 wherein said wax is polyethylene wax having, prior to compaction, an average particle size of no greater than about 15 microns, a maximum particle size of no greater than about 40 microns, and a density in the range of about 0.9 to about 1.4 grams per cc at 25° C.

18. A method of claim 16 wherein said wax is a polyethylene wax that melts at a temperature in the range of about 109° C. to about 111° C.

19. A method of claim 16 wherein said wax is polypropylene wax having, prior to compaction, an average particle size in the range of about 5.0 to about 7.0 microns, a maximum particle size of about 22 microns, and a density in the range of about 0.9 to about 1.4 grams per cc at 25° C.

20. A method of claim 16 wherein said wax is a polypropylene wax that melts at a temperature in the range of about 140° C. to about 143° C., that prior to compaction has an average particle size in the range of about 5.0 to about 7.0 microns, and that prior to compaction has a maximum particle size of about 22 microns.

21. A method of claim 8 wherein the 1,3-dibromo-5,5-dimethylhydantoin being used is in the form of a compacted product formed from 1,3-dibromo-5,5-dimethylhydantoin having an average particle size of at least about 175 microns, and wherein said compacted product was produced using as a binder an amount of a saturated, normally solid, fatty amide effective to form said compacted product.

22. A method of claim 21 wherein the 1,3-dibromo-5,5-dimethylhydantoin used in forming said compacted product had an average particle size of at least about 200 microns.

23. A method of claim 21 wherein the 1,3-dibromo-5,5-dimethylhydantoin used in forming said compacted product had an average particle size of at least about 300 microns.

24. A method of effecting microbiocidal activity in water having a pH of at least about 8.0, which method comprises providing in such water using a 1,3-dibromo-5,5-dimethylhydantoin microbiocidal agent, a microbiocidally effective amount of "free chlorine" that is greater than could be predicted from the amount of "free chlorine" that would be released in said water by an equimolar quantity of N,N'-bromochloro-5,5-dimethylhydantoin, while using a smaller quantity by weight of 1,3-dibromo-5,5-dimethylhydantoin than the quantity by weight of N,N'-bromochloro-5,5-dimethylhydantoin that would be required to release in said water the same microbiocidally effective amount of "free chlorine", wherein the 1,3-dibromo-5,5-dimethylhydantoin being used is in the form of a compacted product produced using as a binder an amount of a micronized synthetic polyethylene wax effective to form said compacted product, said wax having, prior to compaction, an average particle size of no greater than about 15 microns,

a maximum particle size of no greater than about 40 microns, and a density in the range of about 0.9 to about 1.4 grams per cc at 25° C., said wax being compatible with said 1,3-dibromo-5,5-dimethylhydantoin.

25. A method of claim 24 wherein said polyethylene wax melts at a temperature in the range of about 109° C. to about 111° C.

26. A method of effecting microbiocidal activity in water having a pH of at least about 8.0, which method comprises providing in such water using a 1,3-dibromo-5,5-dimethylhydantoin microbiocidal agent, a microbiocidally effective amount of "free chlorine" that is greater than could be released in said water by an equimolar quantity of N,N'-bromochloro-5,5-dimethylhydantoin, while using a smaller quantity by weight of 1,3-dibromo-5,5-dimethylhydantoin than the quantity by weight of N,N'-bromochloro-5,5-dimethylhydantoin that would be required to release in said water the same microbiocidally effective amount of "free chlorine", wherein the 1,3-dibromo-5,5-dimethylhydantoin being used is in the form of a compacted product produced using as a binder an amount of a micronized synthetic polypropylene wax effective to form said compacted product, said wax having, prior to compaction, an average particle size in the range of about 5.0 to about 7.0 microns, a maximum particle size of about 22 microns, and a density in the range of about 0.9 to about 1.4 grams per cc

at 25° C., said wax being compatible with said 1,3-dibromo-5,5-dimethylhydantoin.

27. A method of effecting microbiocidal activity in water having a pH of at least about 8.0, which method comprises providing in such water using a 1,3-dibromo-5,5-dimethylhydantoin microbiocidal agent, a microbiocidally effective amount of "free chlorine" that is greater than could be predicted from the amount of "free chlorine" that would be released in said water by an equimolar quantity of N,N'-bromochloro-5,5-dimethylhydantoin, while using a smaller quantity by weight of 1,3-dibromo-5,5-dimethylhydantoin than the quantity by weight of N,N'-bromochloro-5,5-dimethylhydantoin that would be required to release in said water the same microbiocidally effective amount of "free chlorine", wherein the 1,3-dibromo-5,5-dimethylhydantoin being used is in the form of a compacted product produced using as a binder an amount of a micronized synthetic wax effective to form said compacted product, wherein said wax is a polypropylene wax that melts at a temperature in the range of about 140° C. to about 143° C., that prior to compaction has an average particle size in the range of about 5.0 to about 7.0 microns, and that prior to compaction has a maximum particle size of about 22 microns, said wax being compatible with said 1,3-dibromo-5,5-dimethylhydantoin.

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In re Patent Application of:
Michael Ludensky et al.

Application No.: 10/540,293   Confirmation No.: 8281

Filed: July 20, 2005   Art Unit: 1724

For: METHOD FOR REMOVAL OF BIOFILM   Examiner: P. A. Hruskoci

DECLARATION OF PHILIP G. SWEENY, PH.D. UNDER 37 C.F.R. § 1.132

Exhibit E

Chapter 8: Bleaching

M. LEWIN

INTRODUCTION

The term 'bleaching' includes the obtaining of white cellulosic materials by destroying and removing the encrusting colouring materials, the obtaining of pure cellulose, and sometimes the modification of the properties of the purified cellulose to render it suitable for specific end products.

The main encrusting materials of cellulose are lignin and hemicellulose (hexosans, pentosans and polyuronides (pectic substances) in the case of wood and annual plants, and proteins and polyuronides in the case of cotton.

In the case of sulphite pulp, lignin compounds only are believed to be the coloured products of the pulp [1, 2]. Similarly the dark brown colour of sulphate pulp is composed of condensed sulphur-lignin polymers formed during the cooking [3, 4]. With respect to cotton and flax it has been reported that proteins rich in benzene rings are responsible for the colour [5, 6, 7].

The bleaching is performed either in one oxidative alkaline hypochlorite [8, 9] stage or as a multistage procedure comprising chlorination with chlorine water, hot alkaline extraction and hypochlorite oxidation of the residual lignin. The bleaching should be carried out as mildly as possible in order not to degrade the cellulose and not to decrease its alpha-cellulose content and in order not to produce an excessive amount of carbonyl groups, which reduce the stability of the cellulose in alkaline solutions [10]. The bleaching process thus comprises the following gross reactions: halogenation of lignin, oxidation of cellulose and oxidation of hemicellulose. The bleaching agent employed is consumed in the different reactions according to their relative rates. The rates of these reactions depend not only on the conditions, such as pH, temperature, consistency, concentration and composition of bleaching agent, but to a great extent on the nature of the material to be bleached: the amount and structure of the lignin or lignin sulphonates and the amounts and structure of hemicellulose present. It appears that the rate of the oxidation of the hemicellulose depends greatly on its conformation, as has been lately demonstrated on oxidation of various sugars with bromine [11, 12, 13].

Since the structure and conformation of lignin and hemicellulose in the lignocellulosic materials of the various sources has not been fully elucidated, the bleaching procedures are still largely empirical and the main concern is to utilise the maximum amounts of the bleaching agent for the destruction and solubilisation of the lignin for paper grade pulps and flax and of hemicelluloses for dissolving pulps and cotton.

The earliest recorded reports on the action of bromine on vegetable materials were those of Löwig, Berzelius and of Bolard and Danger [14]. The isolation of cellulose from lignin by alternating extractions with bromine water and ammonia

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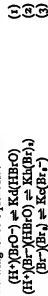
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were reported in 1870 [25]. The few papers published in the following eighty years were concerned with analytical methods for the determination of lignin and cellulose [16, 17, 18, 19].

The information available in the literature on the oxidation of cellulose with hypobromine and bromine is much more limited than for chlorine. The earlier papers dealing with hypobromite oxidation were concerned with the oxidation in strongly alkaline environment and served for comparison with the hypobromite oxycelluloses to celluloses obtained with other oxidants. Clibbens and Ridge [20] found the rate of hypobromite oxidation to be much more rapid than that of hypochlorite oxidation and they used lower concentrations of hypobromite in order to obtain comparable results. The hypobromine oxidation was used [21] to define the 'reactivity ratio' as an alternative to the 'hydrolysis number' of Schwalbe [22]. The reactivity ratio was defined as the ratio of the copper numbers obtained at controlled conditions by hypobromite oxidation of swollen and plain bleached cotton.

The mechanism suggested for the oxidation postulated that first the aldehyde groups are formed and are subsequently oxidised to carboxyls [23]. The authors found a maximum copper number at pH 7, followed by a second smaller maximum at pH 12. The methylene blue absorption reached two nearly equal maxima at pH 7 and 11.2. The fluidities of the oxycelluloses were, however, not determined [23].

Van Fossen and Pacsu [24] oxidised cotton with relatively concentrated alkaline hypobromite and concluded that this oxidation is non-selective, and approaches the form of wet combustion.

The first systematic investigations on the bleaching of pulp and cotton with hypobromite and hypochlorite-bromide solutions have been carried out in Israel since 1943 [25, 26, 27, 28, 29].

The Composition of Hypobromite Solutions. The composition of hypobromite solutions is governed by the following three equilibria:
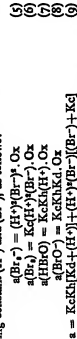
$$(H^+)(BrO^-) \rightleftharpoons Kd(HBrO) \tag{1}$$
$$(H^+)(Br^-)(HBrO) \rightleftharpoons Kh(Br_2) \tag{2}$$
$$(Br^-)(Br_2) \rightleftharpoons Kc(Br_3^-) \tag{3}$$

which are rapidly established (see also this part, Ch. 9).

The hypobromite solutions are therefore composed of four oxidising agents:

$$Ox \quad (BrO^-)+(HBrO)+(Br_2)+(Br_3^-) \tag{4}$$
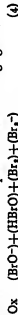
The concentrations of the components may be determined by solving the above equations, assuming constant (H^+) and (Br^-), as follows:

$$a(Br_3^-) = (H^+)(Br^-)\cdot Ox \tag{5}$$
$$a(Br_2) = Kd(H^+)(Br^-)\cdot Ox \tag{6}$$
$$a(HBrO) = KcKd(H^+)\cdot Ox \tag{7}$$
$$a(BrO^-) = KcKhKd\cdot Ox \tag{8}$$

$$a = KcKh[Kd+(H^+)]+(H^+)(Br^-)[(Br^-)+Kc] \tag{9}$$

With the aid of equations (5)–(9) the composition of the solutions over the whole pH-range 0–14 and a wide range of bromide concentrations can be easily calculated

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[30], using the equilibrium constants Kc = 0.063 [31], Kh = 5.8 × 10⁻⁹ [32, 33], and Kd = 2 × 10⁻⁹ [34, 35].

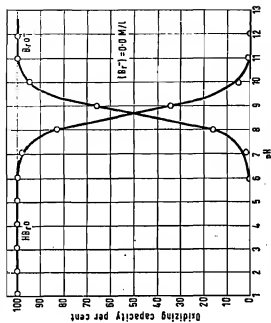
FIG. I *The composition of hypobromite solutions at pH 0–14 and* (Br⁻) = 0·0 M/l
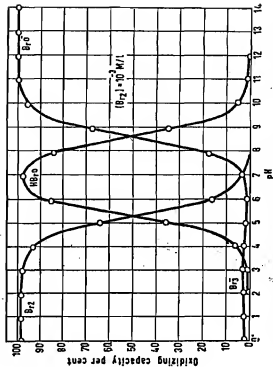
FIG. II *The composition of hypobromite solutions at pH 0–14 and* (Br⁻) = 10⁻³ M/l

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Examples of such calculations for several bromide concentrations are presented in FIGS. I–IV. The system has also been represented by a three-dimensional tetrahedral diagram [36]. It is evident that at low bromide concentrations 0–10⁻⁸ moles per litre the main components of the solution are $HBrO$ and $BrO⁻$ and in water disinfection processes, carried out at these concentrations at the pH range 5–9, hypobromous acid will be virtually the only oxidising species. At the bromide concentration range of $10⁻⁴$–$10⁻³$ which is the bleaching range and at pH values below 8, the solution contains $HBrO$ and Br_2 and only a small percentage of $Br_3⁻$.

The concentrations of Br_2 and $Br⁻$ in the solutions of hypobromite depend on the method of preparation of these solutions. If the solution is prepared by dissolving bromine in alkali,

$$Br_2 + 2NaOH = NaOBr + NaBr \qquad (a)$$

it will contain bromide ions in an amount equal to 50 per cent of the total bromine present. During an oxidation reaction the concentration of $Br⁻$ and subsequently of Br_2 increases owing to the reduction of $HBrO$ or $BrO⁻$ and equilibrium (2), respectively.
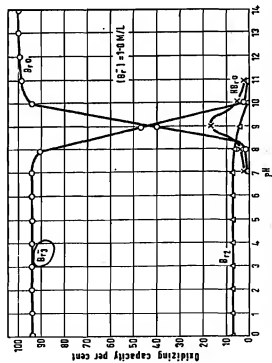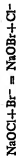

FIG. III. The composition of hypobromite solutions at pH =14 and $(Br⁻) = 1·0\ M/l$

If, however, the hypobromite solution is prepared by the oxidation of bromide with hypochlorite [37, 38]

$$NaOCl + Br⁻ = NaOBr + Cl⁻ \qquad (b)$$

the solution is virtually free of $Br⁻$ and its composition is given by FIG. I. During an oxidation reaction, bromide ions gradually accumulate in the solution. It is evident that for the same initial concentration of total bromine, the solution prepared according to method (b) always contains less than half the bromide ions

present in a solution prepared according to method (a). Since the rate of decomposition of hypobromite solutions [39, 40] increases with the increase of bromide concentration [50, 51], solutions (b) are more stable than solutions (a).

With the increase of the $Br⁻$ concentration above $10⁻⁴$ mole per litre, the concentration of Br_2 increases, the range of pH at which $HOBr$ is present and the percentage of $HOBr$ of the total oxidising capacity decreases. This range of Br_2 concentration is encountered in oxidations of a preparative nature, usually carried out at high concentrations of bromine or hypobromite.
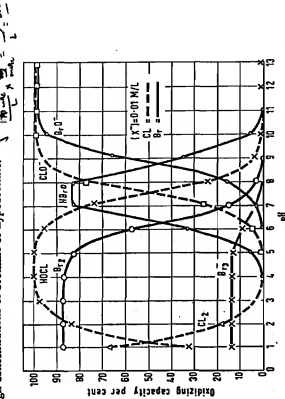

FIG. IV. The composition of hypobromite and of hypochlorite solutions at pH 0–14 and $(X⁻) = 1·0\ M/l$

In FIGS. IV a comparison between the composition of hypochlorite and hypobromite solutions in the whole pH range 0–14, at a halogenide concentration of 0·01 moles per litre is made. For computing the data for hypochlorite, concentration equilibria analogous to (1) and (2) were used, assuming $Kd(Cl) = 1.7 \cdot 10⁻⁴$ [gt] and $Kh(Cl) = 4.8 \cdot 10⁻⁴$ [gz]. It is seen that the maximum of the hypochlorous acid appears at pH 4–5 as compared to pH 7–8 for the hypobromous acid; the range of the predominance of hypobromite ions is located at higher pH values; no $X_3⁻$ ion exists in the case of chlorine and even at pH 1 the oxidant contains 20 per cent of hypochlorous acid.

It may be expected that the differences in composition should bring about differences in oxidising and bleaching action of the two oxidants.

The effective oxidation potentials of the bromine systems are lower than those of the chlorine systems.

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TABLE I
The Oxidation Potentials of Bromine and Chlorine Systems

$2Br^- = Br_2+2e$ E = −1.087 [43]
$Cl^- = Cl_2+2e$ E = −1.40 [43]
$Br^-+H_2O = HBrO+H^+$ E = −1.33 [43]
$Cl^-+H_2O = HClO+H^+$ E = −1.50 [43]
$Br^-+2OH^- = BrO^-+H_2O$ E = −0.75 [43]
$Cl^-+2OH^- = ClO^-+H_2O$ E = −0.90 [43]
$ClO^- = ClO_2+e$ E = −0.95 [44]
$ClO^-+2H_2O = ClO_3^-+4H^++4e$ E = −0.75 [44]

It was stated [45, 46] that the reason for chlorine dioxide and chlorite not attacking the cellulose was their low oxidation potential.

Since these oxidation potentials, as may be seen from TABLE 1, are close to the oxidation potentials of hypobromite, it might have been inferred that hypobromite should behave similarly towards cellulose. This was, however, not found to be the case. As already pointed out by Giertz [9], the oxidation potential cannot be the decisive factor in determining the reaction velocity, although the bleaching agent must have a certain oxidation potential in order to oxidize the cellulose. In spite of the higher oxidation potential of elementary chlorine as compared to HOCl, the latter oxidises the cellulose much more rapidly. Similar results were obtained with Br₂, HOBr and BrO⁻. On the other hand the much higher rate of the oxidation of cellulose by the bromine systems than by the chlorine systems indicates that different factors, such as specific mechanisms of reaction and steric factors influence the reaction rates much more profoundly than the oxidation potentials.

THE HYPOCHLORITE-BROMIDE SYSTEM AT pH VALUES 7-14

BROMIDE IS QUANTITATIVELY converted into hypobromite by oxidation with hypochlorite at the whole pH range 9-14 [38]. The reaction is of second order and proportional to the concentrations of the bromide and hypochlorite. The reaction rate is linearly dependent on the hydrogen ion concentration and the rate determining step was found to be:

$$HOCl+Br^-\rightarrow HOBr+Cl^-$$

At pH values below 10 the oxidation of the bromide is very rapid. An analytical procedure for the determination of bromide in the presence of chloride was based on this reaction [25].
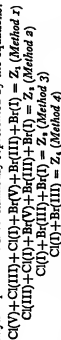
The reaction provides a convenient method for the preparation of bromide-free hypobromite solutions [25]. Equivalent amounts of bromide are added to a hypochloric solution at pH 9-9.5 and at room temperature. After 5 minutes, sodium hydroxide is added to bring the pH to 13, at which the rate of formation of bromite and bromate is low [48, 49, 50, 51].

At pH values 7-9, the formation of hypobromite from bromide and hypochlorite is extremely rapid, but if the hypochlorite is present in excess, other reactions set in which consist of the decomposition of the resulting hypochlorite-hypobromite mixture, yielding chlorate, bromate and chloride as well as bromite and chlorite as intermediates [25, 52].

The analytical chemistry of these complex mixtures is difficult, but an analytical procedure for determining their composition has been described [52]. The procedure utilizes four volumetric methods:

i. The sum of normalities of chlorate Cl(V), chlorite Cl(III), hypochlorite Cl(I), bromate Br(V), bromite Br(III), and hypobromite Br(I) is determined by the ferrous sulphate-permanganate method.

ii. The sum of chlorite, hypochlorite, bromate, bromite and hypobromite is determined by adding to a sample acidified KI and titrating with thiosulphate.

iii. The sum of hypochlorite, bromite and hypobromite is determined by means of the arsenite iodine titration.

iv. The hypochlorite and bromite is determined by the phenol-arsenite-iodine method [48, 53].

The analytical procedure is schematically represented by the equations:

$$Cl(V)+Cl(III)+Cl(I)+Br(V)+Br(III)+Br(I) = Z_1 \quad (Method \ 1)$$
$$Cl(III)+Cl(I)+Br(V)+Br(III)+Br(I) = Z_2 \quad (Method \ 2)$$
$$Cl(I)+Br(III)+Br(I) = Z_3 \quad (Method \ 3)$$
$$Cl(I)+Br(III) = Z_4 \quad (Method \ 4)$$

where all symbols are expressed in moles hypohalic per litre. Thus hypobromite (Z_3-Z_4) and chlorite (Z_2-Z_3) are accurately determined. Besides the concentration of these two components, only the sum of bromate and chlorite (Z_1-Z_2) and the sum of hypochlorite and bromite (Z_4) can be given. However, the ratio of bromate, bromite and hypobromite present in the reaction mixture and expressed in moles is equal at any time to the amount of bromide added initially or to the initial hypobromite concentration:

$$1/3Br(V)+1/2Br(III)+Br(I) = b$$
$$1/3Br(V)+1/2Br(III) = b-b = \Delta Br(I)$$

Since the bromine is determined only together with chlorate (Z_1-Z_4) this equation will change into:

$$[1/3Br(V)+1/2Cl(III)+1/2Br(III)]-1/3Cl(V) = Br(I)$$

If the difference $Br(I)-[1/3Br(V)+1/2Cl(III)+1/2Br(III)]$ is positive, the lower limit of the bromide present in the solution is determined, since the chlorite possibly present will decrease the value of the difference. On the other hand, a negative difference will determine the lower limit of the chlorite present in the solution, since a part of the hypobromite may have yielded bromite and thus a larger part of the titrated quantity Z_1-Z_4 might be attributed to chlorite.

The above analytical procedure enabled the investigation of the reactions occurring in the hypochlorite-hypobromite mixtures as well as the interactions between the halogenides and the hypohalogenites in dilute solutions as used in bleaching operations.